



US006780518B2

(12) **United States Patent**  
**Azechi et al.**

(10) **Patent No.: US 6,780,518 B2**  
(45) **Date of Patent: Aug. 24, 2004**

(54) **SILICONE RUBBER ADHESIVE  
COMPOSITION AND INTEGRALLY  
MOLDED ARTICLE OF SILICONE RUBBER  
AND THERMOPLASTIC RESIN**

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(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 31 days.

(21) Appl. No.: **10/035,213**

(22) Filed: **Jan. 4, 2002**

(65) **Prior Publication Data**

US 2002/0132891 A1 Sep. 19, 2002

(30) **Foreign Application Priority Data**

Jan. 5, 2001 (JP) ..... 2001-000536

(51) **Int. Cl.<sup>7</sup>** ..... **B32B 7/10**; B32B 27/08;  
B32B 5/00; C08L 83/05; C08L 83/06

(52) **U.S. Cl.** ..... **428/451**; 428/409; 428/413;  
524/858; 524/860; 524/861; 524/868; 525/476;  
525/478; 528/31; 528/33; 528/40; 264/255

(58) **Field of Search** ..... 428/446, 447,  
428/448, 409, 413, 451; 524/858, 860,  
861, 863, 868; 528/31, 33, 40; 525/474,  
476, 478; 264/241, 250, 255

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

4,582,762 A	4/1986	Onohara et al.
4,686,124 A	8/1987	Onohara et al.
4,814,231 A	3/1989	Onohara et al.
4,834,721 A	5/1989	Onohara et al.
4,916,038 A	4/1990	Lau et al.

5,405,896 A	4/1995	Fujiki et al.	
5,530,075 A *	6/1996	Morita et al.	525/431
5,536,803 A	7/1996	Fujiki et al.	
5,714,265 A *	2/1998	Meguriya et al.	428/413
5,879,809 A	3/1999	Muramatsu et al.	
5,989,704 A	11/1999	Hashimoto et al.	
2002/0028335 A1 *	3/2002	Fujiki et al.	428/447
2002/0032270 A1 *	3/2002	Azechi	524/492

**FOREIGN PATENT DOCUMENTS**

EP	0 276 790 B1	6/1994
EP	1026217 A1	8/2000
EP	1172413 A2	1/2002
EP	1172414 A2	1/2002
JP	63-183843 A	7/1988
JP	63-045292 B2	9/1988
JP	2-34311 B2	8/1990
JP	6-172738 A	6/1994
JP	8-53661 A	2/1996
JP	9-165516 A	6/1997
JP	9-165517 A	6/1997

\* cited by examiner

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(57) **ABSTRACT**

A silicone rubber adhesive composition comprising (A) a heat curable organopolysiloxane composition of the addition curing type or peroxide curing type, (B) reinforcing silica fines, and (C) an organic compound or organosilicon compound having an epoxy equivalent of 100–5,000 g/mol and containing at least one aromatic ring in a molecule is easily moldable within a short time by injection molding, suitable in primerless molding, and bondable with various thermoplastic resins. Integrally molded articles in which the silicone rubber adhesive composition is firmly bonded to the thermoplastic resin are obtainable without a need for modification of the resin.

**10 Claims, 6 Drawing Sheets**

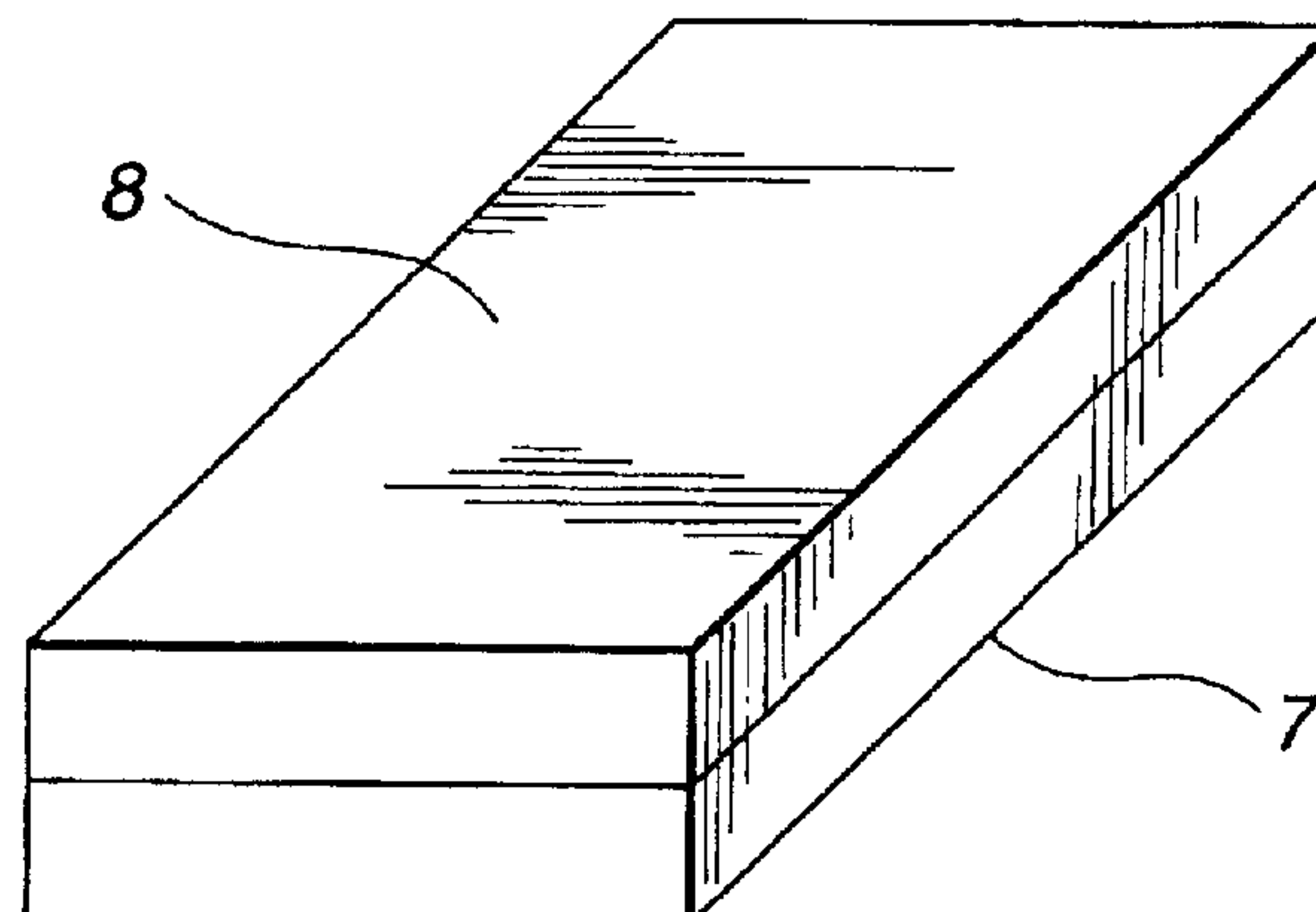


FIG.1A

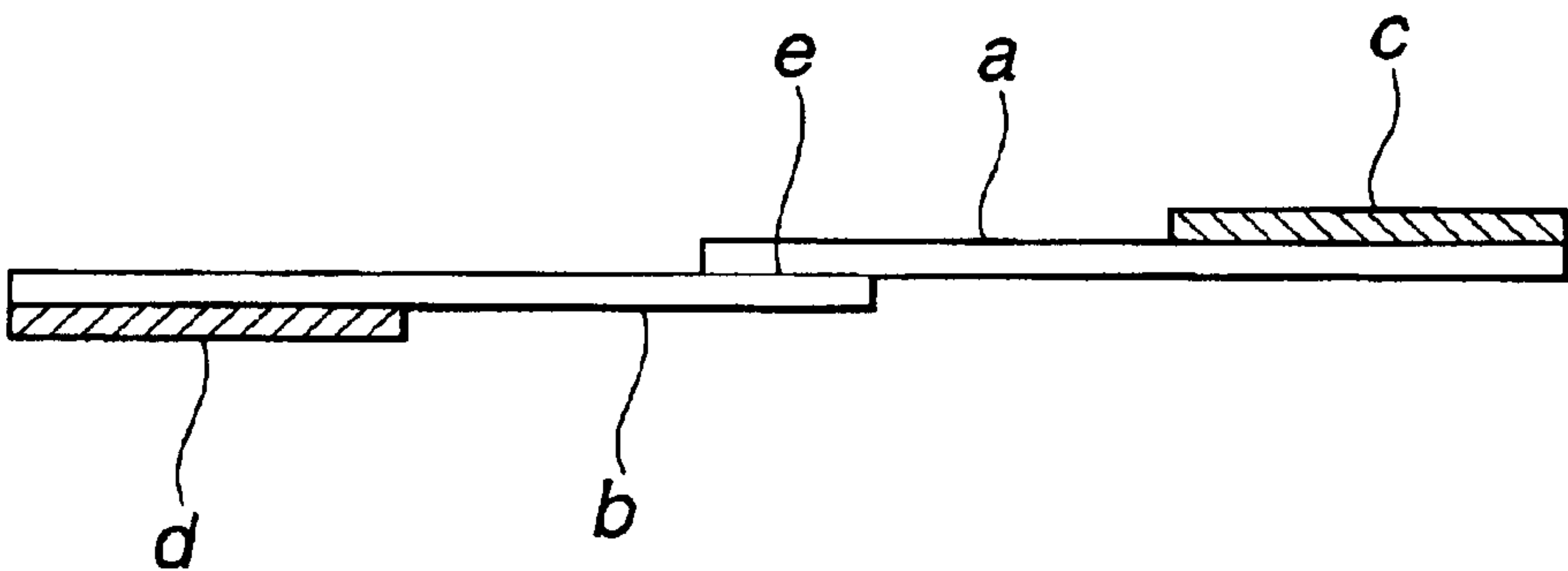


FIG.1B

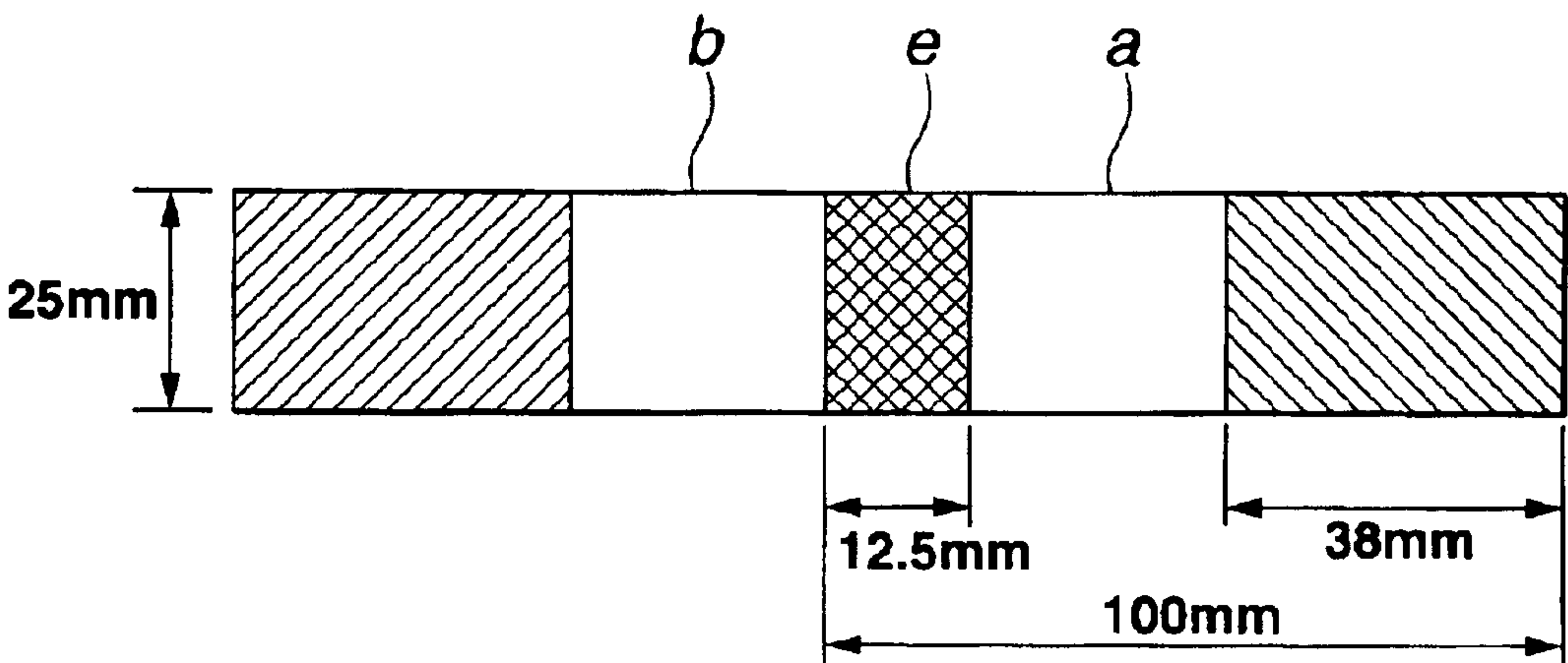


FIG.2

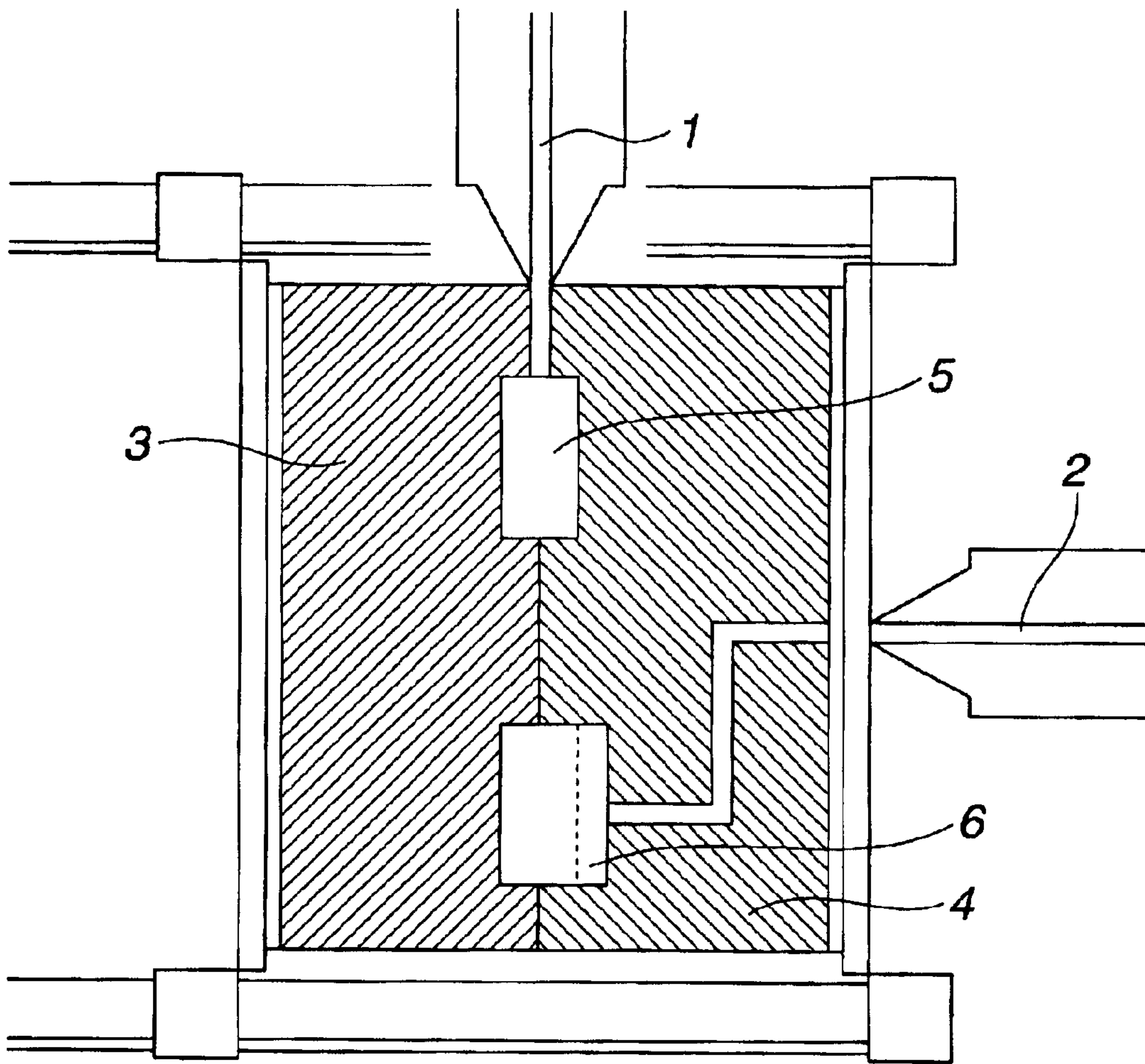




FIG.3

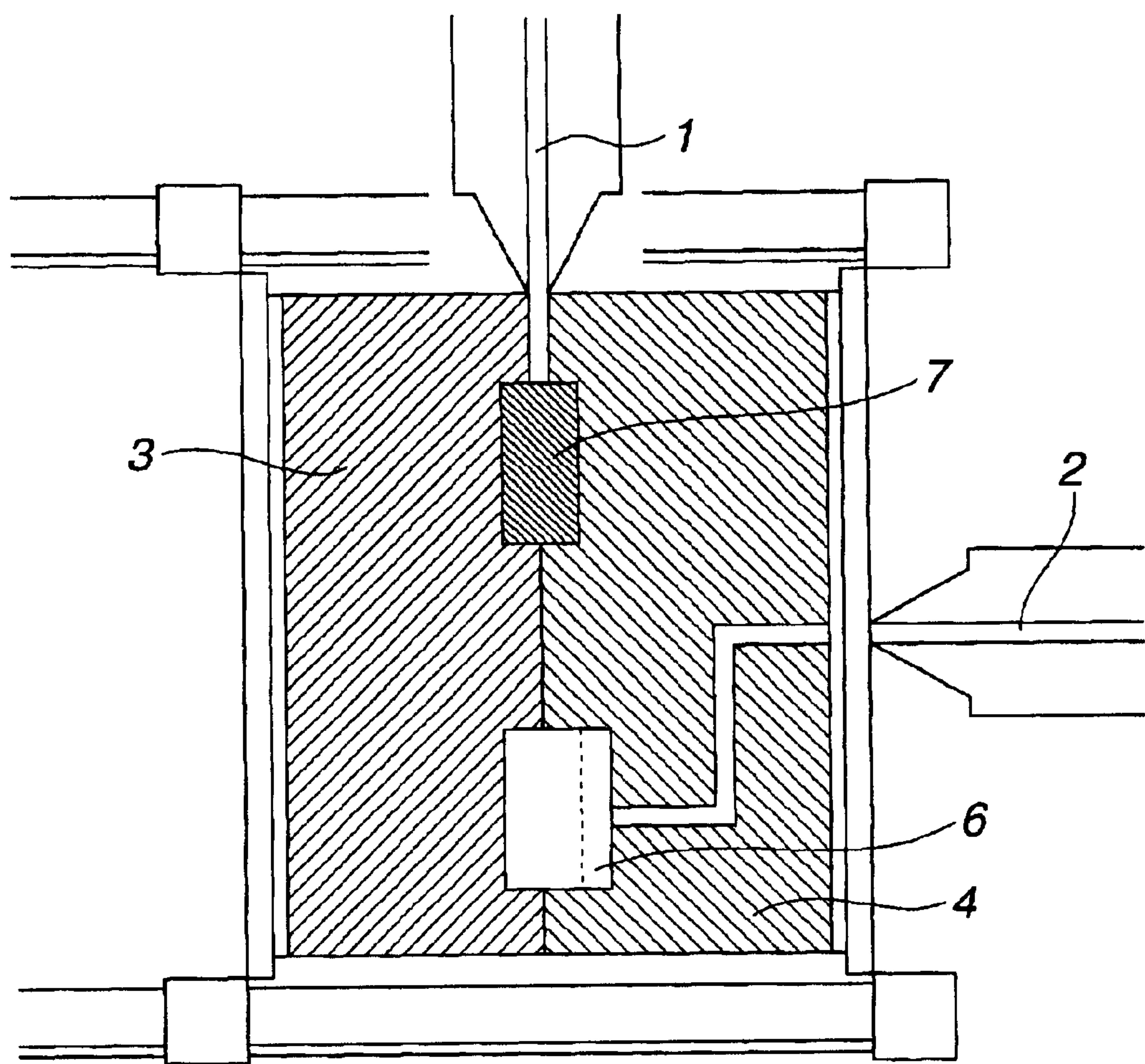


FIG.4

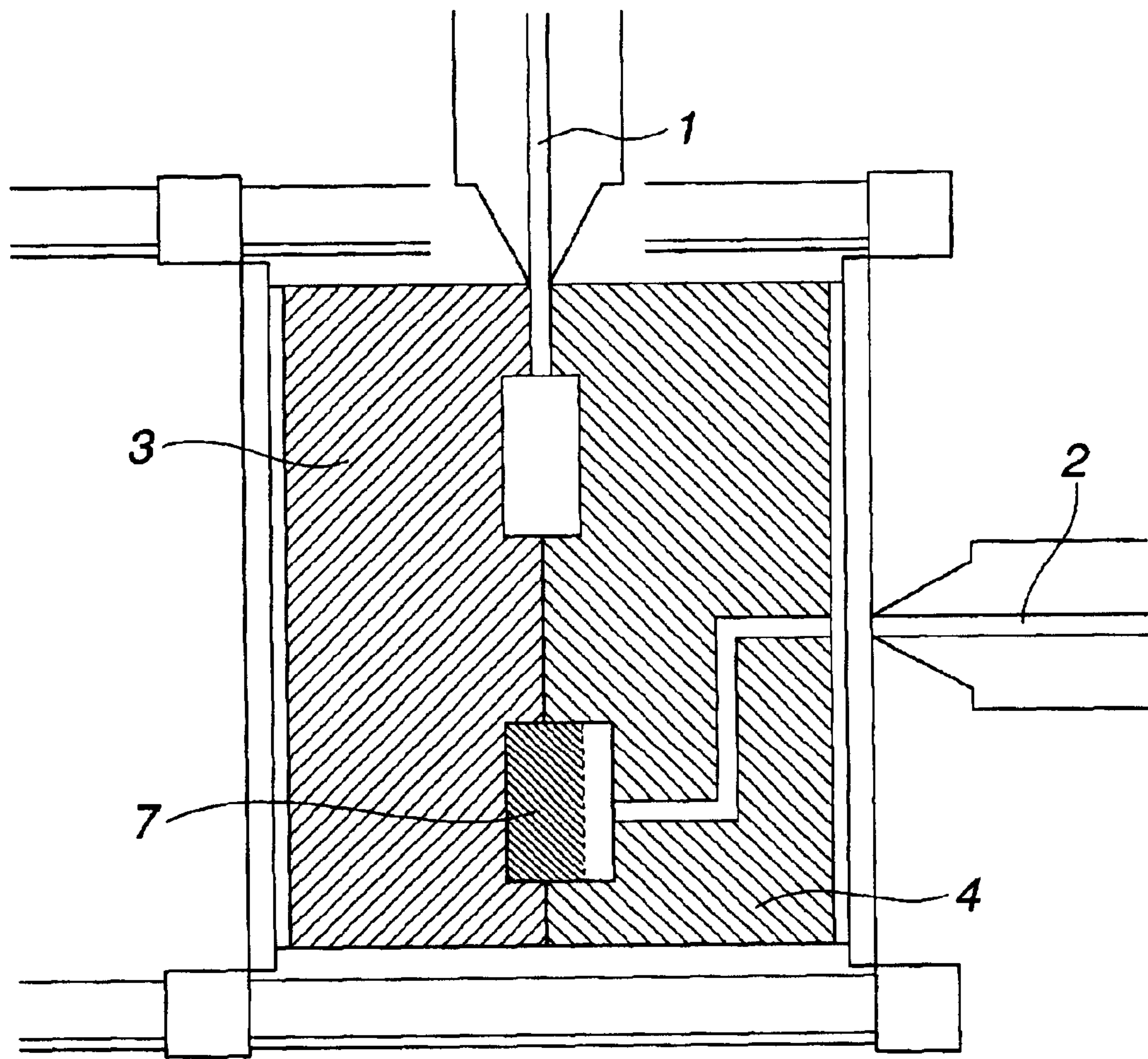
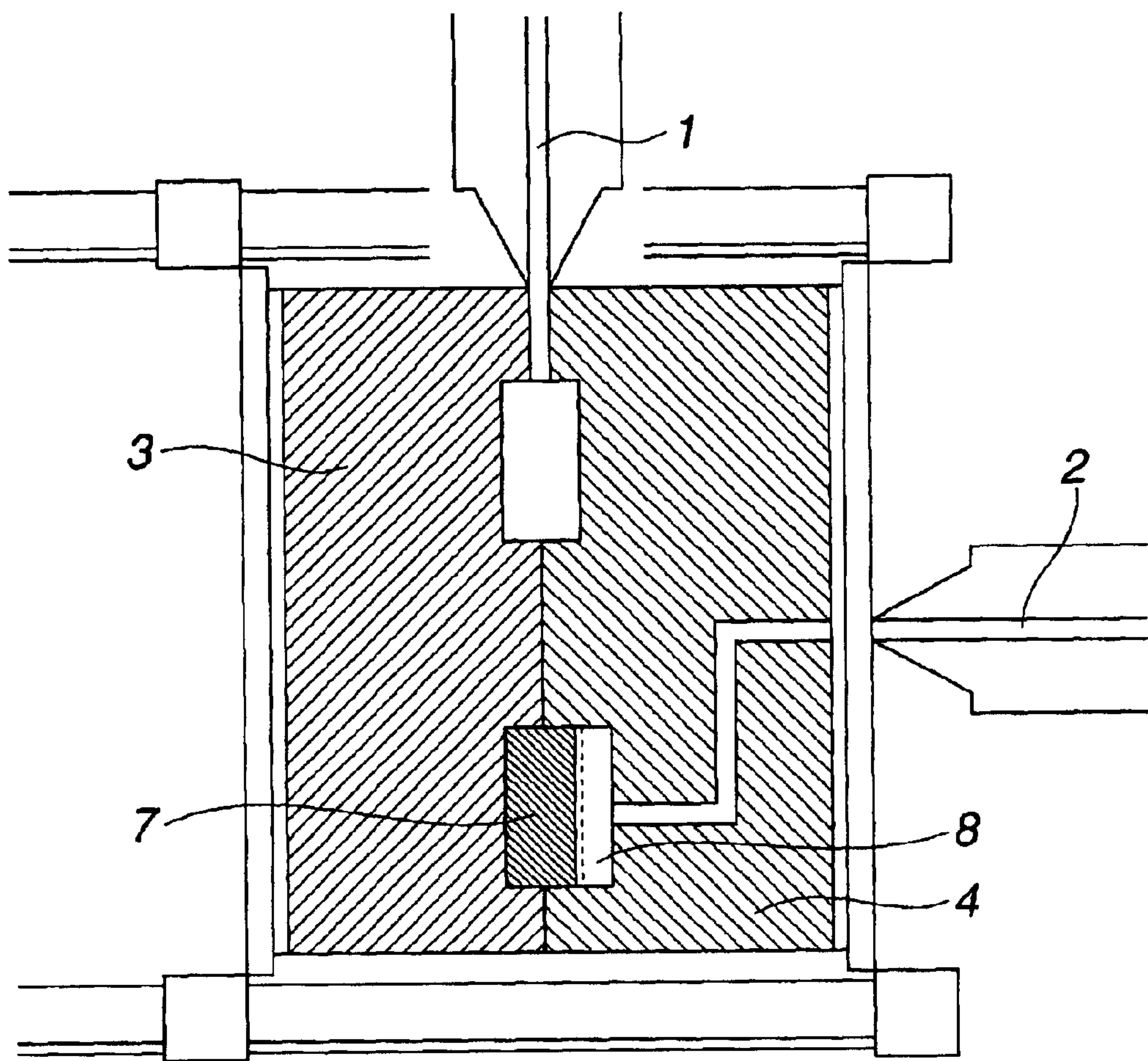
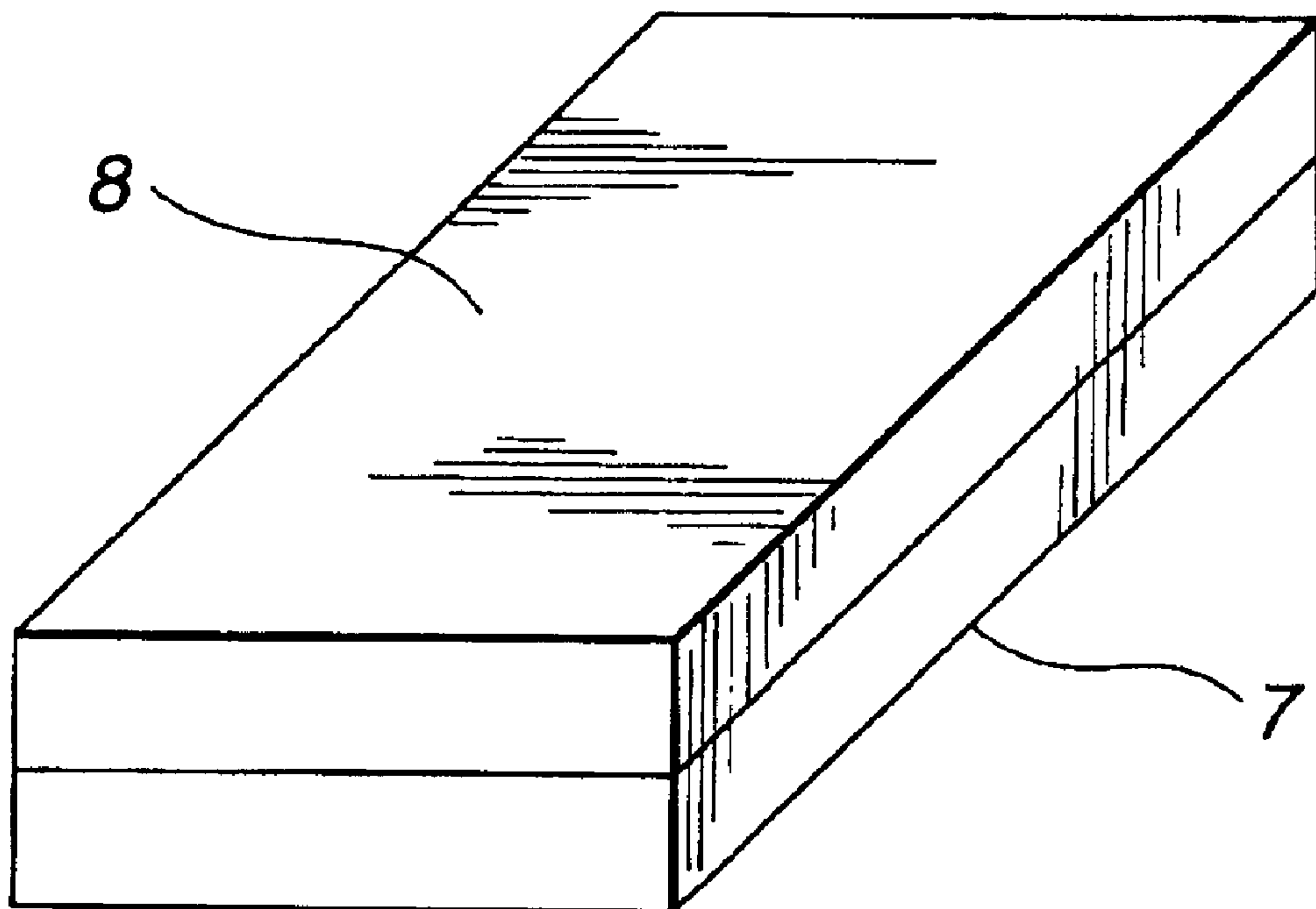


FIG.5



**FIG.6**





# **SILICONE RUBBER ADHESIVE COMPOSITION AND INTEGRALLY MOLDED ARTICLE OF SILICONE RUBBER AND THERMOPLASTIC RESIN**

This invention relates to a silicone rubber adhesive composition which can be simply and briefly molded by injection molding, extrusion or mechanical application using a robot, is suited for primerless molding and hence, integral molding with a thermoplastic resin, and exhibits the unique nature that when molded together with a thermoplastic resin in a mold which has been or has not been surface treated as by chromium plating, the composition is adherent only to the resin, but not to the mold. It also relates to an integrally molded article of a cured product (silicone rubber) of a silicone rubber adhesive composition bonded to a thermoplastic resin.

## **BACKGROUND ART**

Nowadays silicone rubber, due to its excellent characteristics, finds widespread use in a variety of fields including electric, electronic, automotive and building fields. The demands for the silicone rubber in these fields include workability, seal and insulation during assembly. In some applications where the adhesion of silicone rubber to resins is necessary, adhesion is achieved by way of primers. The process requires the step of applying primer and is thus cumbersome. One solution is a self-adhesive type silicone rubber obtained by adding an adhesive to a silicone rubber composition. The self-adhesive type silicone rubber eliminates the application step, shortens the operating time, reduces the cost, and improves the efficiency of operation. It is effective in manufacturing integrally molded articles with resins.

In connection with the primerless molding of addition type heat-curable silicone rubber, a number of reports have been made for bonding silicone rubber to organic resins. In one exemplary attempt, self-adhesive type silicone rubber material is cured on resins. A number of proposals have been made relating to specific adhesive components for use in the self-adhesive type silicone rubber. Also, JP-B 2-34311 corresponding to U.S. Pat. Nos. 4,582,762, 4,686,124, 4,814,231 and 4,834,721 discloses to add an organopolysiloxane containing at least 30 mol % of hydrogen atoms directly bonded to silicon atoms to an organic resin whereby the resin is bondable to an addition curing type silicone rubber. JP-B 63-45292 discloses the integration of silicone rubber to organic resin by physical engagement. JP-A 63-183843 corresponding to EP 276,790 discloses the integral adhesion of silicone rubber to an olefin resin having grafted thereto a compound having an aliphatic unsaturated group and a silicon atom-bonded hydrolyzable group. JP-A 9-165516 corresponding to U.S. Pat. No. 5,879,809 and JP-A 9-165517 corresponding to U.S. Pat. No. 5,989,704 of Shin-Etsu Chemical Co., Ltd. propose a process in which a thermoplastic resin having added thereto a compound having unsaturated groups and hydrogen atoms directly bonded to silicon atoms is adhesively joined and integrated with silicone rubber as well as an integrally molded article in which a thermoplastic resin having blended therein a thermoplastic oligomer containing aliphatic unsaturated groups is integrally molded with an oil-bleeding silicone rubber.

However, heat curable silicone rubber of the addition type fails to achieve within brief molding a sufficient bond to general thermoplastic resins, fibers and films, such as ABS, PPO, PPS, PC, PE, PP, PBT, acrylic resins, phenolic resins,

polyimide resins, PA and aromatic PA and other copolymers in resin, fiber or film form. To acquire a bonding ability, the resins must be modified as suggested in the above patents. Modification of resins requires extra steps and an increased cost, and the modified resins sometimes become susceptible to quality alteration. Even if a bond is established without resin modification, there still arises a problem that when an integrated silicone rubber/resin article is formed in a mold, the molded article sticks to the mold. In particular, none of available silicone rubber compositions fully satisfy the requirements when combined with polyamide resins and fibers. It remains of interest to develop an integrally molded article of thermoplastic resin and silicone rubber which when formed in a mold, does not stick to the mold and establishes a firm bond between the thermoplastic resin and the silicone rubber.

## **SUMMARY OF THE INVENTION**

An object of the invention is to provide a silicone rubber adhesive composition which can be firmly integrated with thermoplastic resins, as well as an integrally molded article thereof with a thermoplastic resin.

It has been found that blending an organopolysiloxane composition of the heat curing type with an organic compound or organosilicon compound containing an amount of epoxy group to give an epoxy equivalent of 100 to 5,000 g/mol and at least one aromatic ring in a molecule affords a silicone rubber adhesive composition which is firmly bondable to thermoplastic resins. When this silicone rubber adhesive composition is molded and joined with a thermoplastic resin, there is obtained an integrally molded article in which the silicone rubber is firmly bonded to the thermoplastic resin. Even under brief curing conditions using an injection molding technique, the silicone rubber adhesive composition develops a sufficient bonding force to the thermoplastic resin. The integrally molded article of silicone rubber/thermoplastic resin can be released from the mold in a practically acceptable way. The silicone rubber adhesive composition is effective even to highly crystalline polyamide resins and fibers such as nylon 66 and aromatic polyamides.

The invention provides a silicone rubber adhesive composition comprising (A) 100 parts by weight of a heat curable organopolysiloxane composition, (B) 1 to 100 parts by weight of reinforcing silica fines, and (C) 0.1 to 50 parts by weight of an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule. In a preferred embodiment, component (C) is an organosilicon compound containing at least one Si—H group in a molecule. The composition most often provides a greater bond strength to organic resins than to metals.

Also contemplated herein is an integrally molded article comprising the cured silicone rubber adhesive composition (i.e., silicone rubber) and a thermoplastic resin.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 illustrates a bond strength test specimen, FIG. 1A being a cross-sectional view and FIG. 1B being a plan view.

FIG. 2 is a schematic view of a two-color injection molding machine.

FIG. 3 is a view similar to FIG. 2, showing the resin injected into a first cavity.

FIG. 4 is a view similar to FIG. 2, showing the molded resin sheet set in a second cavity.



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FIG. 5 is a view similar to FIG. 2, showing the silicone rubber composition injected into the second cavity.

FIG. 6 is a perspective view of the resulting composite body of resin and rubber sheets.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The silicone rubber adhesive composition of the invention includes as essential components, (A) a heat curable organopolysiloxane composition, (B) reinforcing silica fines, and (C) an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule.

Component (A) is a heat curable organopolysiloxane composition which may be either an addition reaction curing type organopolysiloxane composition or an organic peroxide curing type organopolysiloxane composition, with the former being preferred.

The addition reaction curing type organopolysiloxane composition is preferably defined as comprising (1) 100 parts by weight of an organopolysiloxane having on the average at least two alkenyl groups in a molecule, (2) 0.1 to 50 parts by weight of an organohydrogenpolysiloxane having on the average at least two hydrogen atoms attached to silicon atoms in a molecule, and (3) a catalytic amount of an addition reaction catalyst.

The organic peroxide curing type organopolysiloxane composition is preferably defined as comprising (i) 100 parts by weight of an organopolysiloxane having on the average at least two alkenyl groups in a molecule, and (ii) a catalytic amount of an organic peroxide.

In the addition reaction curing type organopolysiloxane composition, the organopolysiloxane having on the average at least two alkenyl groups in a molecule as component (1) is typically represented by the following average compositional formula (1):



wherein  $R^1$ , which may be the same or different, is a substituted or unsubstituted monovalent hydrocarbon group of 1 to 12 carbon atoms, preferably 1 to 8 carbon atoms, and "a" is a positive number of 1.5 to 2.8, preferably 1.8 to 2.5, and more preferably 1.95 to 2.05.

Examples of the substituted or unsubstituted monovalent hydrocarbon groups attached to silicon atoms, represented by  $R^1$ , include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, cyclohexyl, octyl, nonyl and decyl; aryl groups such as phenyl, tolyl, xylyl and naphthyl; aralkyl groups such as benzyl, phenylethyl and phenylpropyl; alkenyl groups such as vinyl, allyl, propenyl, isopropenyl, butenyl, hexenyl, cyclohexenyl and octenyl; and substituted ones of the foregoing groups in which some or all of the hydrogen atoms are replaced by halogen atoms (e.g., fluoro, bromo and chloro), cyano groups or the like, such as chloromethyl, chloropropyl, bromoethyl, trifluoropropyl and cyanoethyl.

At least two of the  $R^1$  groups must be alkenyl groups, preferably of 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms. It is noted that the content of alkenyl groups is preferably 0.001 to 20 mol %, especially 0.01 to 10 mol % based on the entire organic groups attached to silicon atoms (that is, the substituted or unsubstituted monovalent hydrocarbon groups included as  $R^1$  in formula (1)). The alkenyl groups may be attached to silicon atoms at ends of the molecular chain and/or silicon atoms midway the

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molecular chain. When the cure rate of the composition and the physical properties of cured parts are taken into account, the organopolysiloxane should preferably have at least alkenyl groups attached to the silicon atoms at molecular chain ends. The preferred groups represented by  $R^1$  other than the alkenyl groups are alkyl groups such as methyl, aryl groups such as phenyl, and fluoroalkyl groups such as trifluoropropyl.

With respect to the structure, the organopolysiloxane is generally a diorganopolysiloxane of a basically straight chain structure whose backbone is comprised of recurring diorganosiloxane units  $R^1_2SiO_{2/2}$  and which is blocked with a triorganosiloxy group  $R^1_3SiO_{1/2}$  at either end of the molecular chain. However, it may have a partially branched or cyclic structure containing  $R^1SiO_{3/2}$  and/or  $SiO_{4/2}$  units. The alkenyl group-containing organopolysiloxane may have any desired degree of polymerization or viscosity, and encompasses from ones having a low degree of polymerization which are liquid at room temperature (25° C.) to gum-like ones having a high degree of polymerization. Often, the organopolysiloxane used herein has an average degree of polymerization (weight average degree of polymerization) of about 10 to 10,000, preferably about 50 to 10,000, more preferably about 100 to 10,000, and most preferably about 100 to 2,000. With an average degree of polymerization of less than 10, the cured rubber sometimes has unsatisfactory physical properties. It is noted that the organopolysiloxane preferably has a viscosity of about 100 to 1,000,000 centipoise at 25° C., and more preferably about 500 to 500,000 centipoise at 25° C.

As component (2), the organohydrogenpolysiloxane is typically represented by the following average compositional formula (2):



and should have at least two (generally 2 to about 300), preferably at least three, and more preferably 3 to about 150, silicon atom-attached hydrogen atoms (Si—H groups).

In formula (2),  $R^2$  is a substituted or unsubstituted monovalent hydrocarbon group of 1 to 12 carbon atoms, examples of which are as described for  $R^1$  in formula (1). Hydrocarbon groups free of aliphatic unsaturation are preferred, with alkyl groups such as methyl being especially preferred. The letter b is a positive number of 0.7 to 2.1, c is a positive number of 0.001 to 1, and b+c is 0.8 to 3. Preferably, b is 1 to 2, c is 0.01 to 1, and b+c is 1.5 to 2.8.

At least two, preferably at least three Si—H groups in the molecule may be positioned at ends and/or midway of the molecular chain. The molecular structure of organohydrogenpolysiloxane polysiloxane may be straight, cyclic, branched or three-dimensional network. Desirable are those which are liquid at room temperature (25° C.) and have a number of silicon atoms per molecule or a degree of polymerization in the range of about 2 to about 300, more desirably about 3 to about 150. It is noted that the organohydrogenpolysiloxane preferably has a viscosity of about 0.1 to 10,000 centipoise at 25° C., and more preferably about 0.5 to 5,000 centipoise at 25° C.

Exemplary organohydrogenpolysiloxanes of formula (2) include 1,1,3,3-tetramethyldisiloxane, methylhydrogencyclo-polysiloxane, polysiloxane, methylhydrogensiloxane-dimethylsiloxane cyclic copolymers, both end trimethylsiloxy-blocked methylhydrogen-polysiloxane, both end trimethylsiloxy-blocked dimethyl-siloxane-methylhydrogensiloxane copolymers, both end dimethylhydrogensiloxy-blocked dimethylpolysiloxane, both end dimethylhydrogensiloxy-



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blocked dimethylsiloxane-methylhydrogensiloxane copolymers, both end trimethylsiloxy-blocked methylhydrogensiloxane-diphenylsiloxane copolymers, both end trimethylsiloxy-blocked methylhydrogensiloxane-diphenylsiloxane-dimethylsiloxane copolymers, both end dimethylhydrogensiloxy-blocked methylhydrogensiloxane-dimethylsiloxane-diphenylsiloxane copolymers, copolymers of  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  units,  $(\text{CH}_3)_3\text{SiO}_{1/2}$  units, and  $\text{SiO}_{4/2}$  units, copolymers of  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  units and  $\text{SiO}_{4/2}$  units, and copolymers of  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  units,  $\text{SiO}_{4/2}$  units, and  $(\text{C}_6\text{H}_5)_3\text{SiO}_{1/2}$  units.

The organohydrogenpolysiloxane (2) is blended in an amount of 0.1 to 300 parts, preferably 0.3 to 200 parts and more preferably 0.5 to 100 parts by weight per 100 parts by weight of the organopolysiloxane (1). Differently stated, the organohydrogenpolysiloxane (2) is blended in such an amount that about 0.3 to 20 mol, preferably about 0.5 to 5 mol, more preferably about 0.8 to 3 mol, and most preferably about 0.8 to 2.5 mol of silicon atom-attached hydrogen atoms (Si—H groups) in component (2) are available per mol of silicon atom-attached alkenyl groups in component (1).

Component (3) is an addition reaction catalyst. Platinum group metal catalysts are typical, including platinum catalysts, for example, platinum black, platinum chloride, chloroplatinic acid, reaction products of chloroplatinic acid with monohydric alcohols, complexes of chloroplatinic acid with olefins, and platinum bisacetoacetate, palladium catalysts, and rhodium catalysts. The addition reaction catalyst (3) is used in a catalytic amount, typically about 0.1 to 1,000 parts, preferably about 0.5 to 1,000 parts, and more preferably about 1 to 500 parts by weight of platinum group metal per million parts by weight of components (1) and (2) combined.

The addition reaction curing type organopolysiloxane composition is comprised of components (1), (2) and (3) as mentioned above.

Reference is now made to the organic peroxide curing type organopolysiloxane composition. The organopolysiloxane having on the average at least two alkenyl groups in a molecule used herein as component (i) may be the same as component (1) defined above.

The organic peroxide (ii) used herein may be selected from conventional well-known ones, for example, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, p-methylbenzoyl peroxide, o-methylbenzoyl peroxide, 2,4-dicumyl peroxide, 2,5-dimethyl-bis(2,5-t-butylperoxy)hexane, di-t-butyl peroxide, t-butyl perbenzoate, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, and 1,6-bis(t-butylperoxy-carboxy) hexane.

The organic peroxide is used in a catalytic amount, usually 0.01 to 10 parts and preferably 0.1 to 10 parts by weight per 100 parts by weight of the organopolysiloxane (i).

The organic peroxide curing type organopolysiloxane composition is comprised of components (i) and (ii) as mentioned above.

The reinforcing silica fines (B) may be any of silica species commonly used in the art as a reinforcement for rubber.

Although any of silica species used in conventional silicone rubber compositions is useful, reinforcing silica fines having a specific surface area of at least  $50 \text{ m}^2/\text{g}$  are preferred. It is advantageous to use precipitated silica, fumed silica and fired silica having a specific surface area of 50 to  $400 \text{ m}^2/\text{g}$ , with the fumed silica being especially advantageous for improved rubber strength. The reinforcing silica

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fines may be hydrophobized on surfaces with organosilicon compounds and other surface treating agents.

It is recommended that silica fines be previously treated directly in powder form. Any of well-known techniques may be used for the surface treatment. For example, untreated silica fine powder and a surface treating agent are admitted into a mechanical milling device closed under atmospheric pressure or a fluidized bed where they are mixed to effect surface treatment at room temperature or elevated temperature, optionally in the presence of an inert gas. If desired, a catalyst is used to promote the surface treatment. After thorough admixing, the powder is dried. The amount of the surface treating agent used is at least the theoretical amount calculated from the surface area to be covered with the agent.

Suitable treating agents include organosilazanes such as hexamethyldisilazane and divinyltetramethyldisilazane; silane coupling agents, for example, organoalkoxysilanes such as methyltrimethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, butyltrimethoxysilane, dimethyldimethoxysilane, diethyldimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, trimethylmethoxysilane, triethylmethoxysilane, vinyltris(methoxyethoxy)silane, trimethylchlorosilane, dimethyldichlorosilane, divinylmethoxysilane and chloropropyltrimethoxysilane; and organosilicon compounds, for example, organopolysiloxanes such as polydimethylsiloxane and organohydrogenpolysiloxane. After surface treatment with such treating agents, the resulting hydrophobic silica fines are ready for use. Of these treating agents, the silane coupling agents and silazanes are preferred.

An appropriate amount of component (B) blended is 1 to 100 parts, more preferably 2 to 80 parts by weight per 100 parts by weight of component (A). Less amounts of component (B) fail to provide mechanical strength whereas excessive amounts of component (B) are difficult to fill, aggravating working and processing efficiency.

It is recommended that when the surface treated (hydrophobic) silica fines are admixed with component (A), the silica fines be further subjected to a hydrophobic treatment. That is, a second surface treating agent is used in the admixing step for imparting additional hydrophobic property to the once hydrophobized silica fines. Examples of the second surface treating agent include silane coupling agents and partial hydrolyzates thereof, organosilazanes, titanate coupling agents, organopolysiloxane fluids, and organohydrogenpolysiloxane fluids.

The second surface treating agents used herein are described in further detail. Exemplary silane coupling agents used herein are organoalkoxysilanes including methyltrimethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, butyltrimethoxysilane, dimethyldimethoxy-silane, diethyldimethoxysilane, vinyltriethoxysilane, vinyl-trimethoxysilane, trimethylmethoxysilane, triethylmethoxy-silane, vinyltris(methoxyethoxy)silane, trimethylchloro-silane, trimethylaminosilane, glycidoxypropyltrimethoxysilane, glycidoxypropylmethyldiethoxysilane, (epoxycyclohexyl) hexyl)ethyltrimethoxysilane, methacryloxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, dimethyldimethoxysilane, divinylmethoxysilane, and chloropropyltrimethoxysilane. Other silanes are also useful. Partial hydrolyzates of these silanes are also useful.

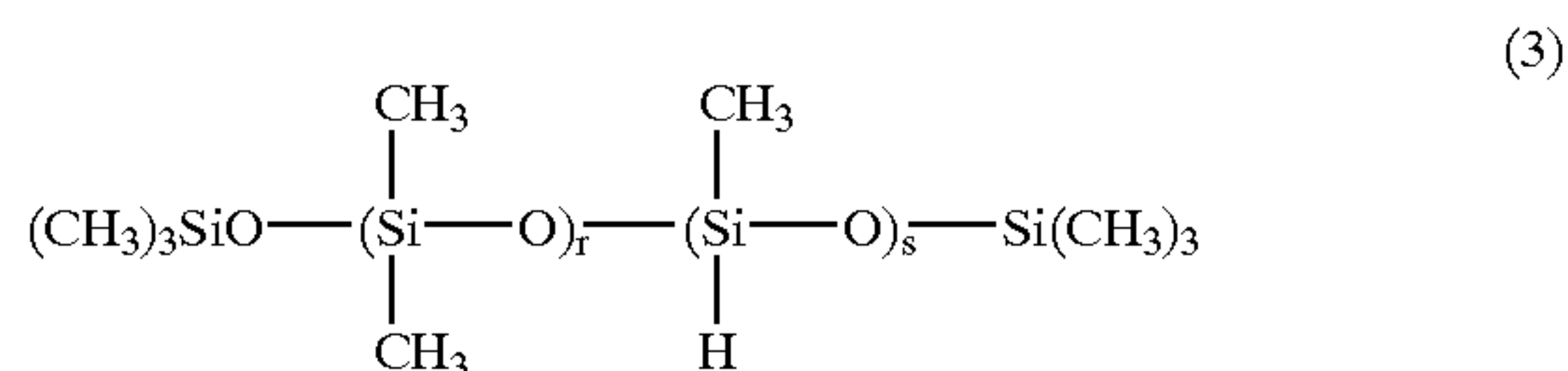
Exemplary organosilazanes used herein are hexamethyldisilazane, divinyltetramethyldisilazane and diphenyltetramethyldisilazane.



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Exemplary titanate coupling agents used herein include tetraisopropyl titanate, tetra-n-butyl titanate, butyl titanate dimer, tetrastearyl titanate, triethanolamine titanate, titanium acetylacetonate, titanium ethylacetoacetate, titanium lactate, octylene glycol titanate, isopropyl tristearoyl titanate, isopropyl tridodecylbenzenesulfonyl titanate, isopropyl tris (dioctylpyrophosphate) titanate, bis(dioctylpyrophosphate) oxyacetate titanate, and bis(dioctylpyrophosphate) ethylene titanate.

The organopolysiloxane fluids used herein may be cyclic, linear, branched or network although linear or cyclic dimethylpolysiloxanes having a viscosity of 0.65 to 100,000 centistokes at 25° C. are preferred. The organohydrogenpolysiloxane fluids used herein may have any of cyclic, linear, branched and network molecular structures. Linear methylhydrogenpolysiloxanes of the following average formula (3) are desirably used.



In the formula, r is an integer of 0 to 50, and s is an integer of 1 to 50. Siloxanes with r in excess of 50 are too viscous and difficult to treat therewith. Similarly, siloxanes with s in excess of 50 are too viscous and difficult to wet the surface.

The amount of the second surface treating agent used is at least the theoretical amount calculated from the surface area to be covered with the agent although amounts less than the theory are acceptable if no problems arise. Specifically, less than 0.1 parts by weight of the second agent per 100 parts by weight of the silica fines is ineffective whereas more than 20 parts by weight of the second agent is wasteful and adds to the cost. For this reason, 0.1 to 20 parts, especially 0.5 to 10 parts by weight of the second surface treating agent is preferably used per 100 parts by weight of the silica fines.

The second surface treatment may be effected on the silica fines as an independent step or together with the step of mixing with other components. Any of well-known techniques for surface treatment may be used. For example, the treated silica fine powder, other components and the second surface treating agent are admitted into a mechanical milling device under atmospheric pressure where they are mixed to effect surface treatment at room temperature or elevated temperature, optionally in the presence of an inert gas. If desired, a catalyst is used to promote the surface treatment.

An organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule is component (C) essential for imparting adhesion, also referred to as tackifier component.

It should contain at least one, preferably 1 to 20, aromatic ring (e.g., benzene ring, naphthalene ring, anthracene ring) in a molecule. The inclusion of an aromatic ring in the

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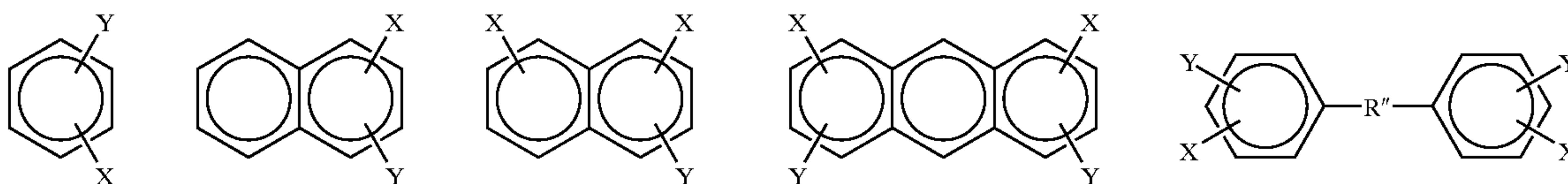
molecule reduces compatibility with component (A) and improves adhesion at the rubber/resin interface. If component (C) is compatible with component (A), it is likely that more of this tackifier component is localized within the rubber component, adversely affecting adhesion to resins. It is thus recommended that component (C) be semi-compatible or incompatible with component (A).

The organic or organosilicon compound should also have at least one epoxy group (e.g., glycidoxy) in the molecule. The epoxy group such as glycidoxy is necessary for the compound to develop adhesion. The epoxy equivalent is in the range of 100 to 5,000 g/mol, and preferably 120 to 4,000 g/mol. An epoxy equivalent below 100 g/mol leads to difficulty of synthesis, too poor compatibility with the silicone rubber composition, and detrimental effects on rubber physical properties. An epoxy equivalent in excess of 5,000 g/mol leads to insufficient adhesion.

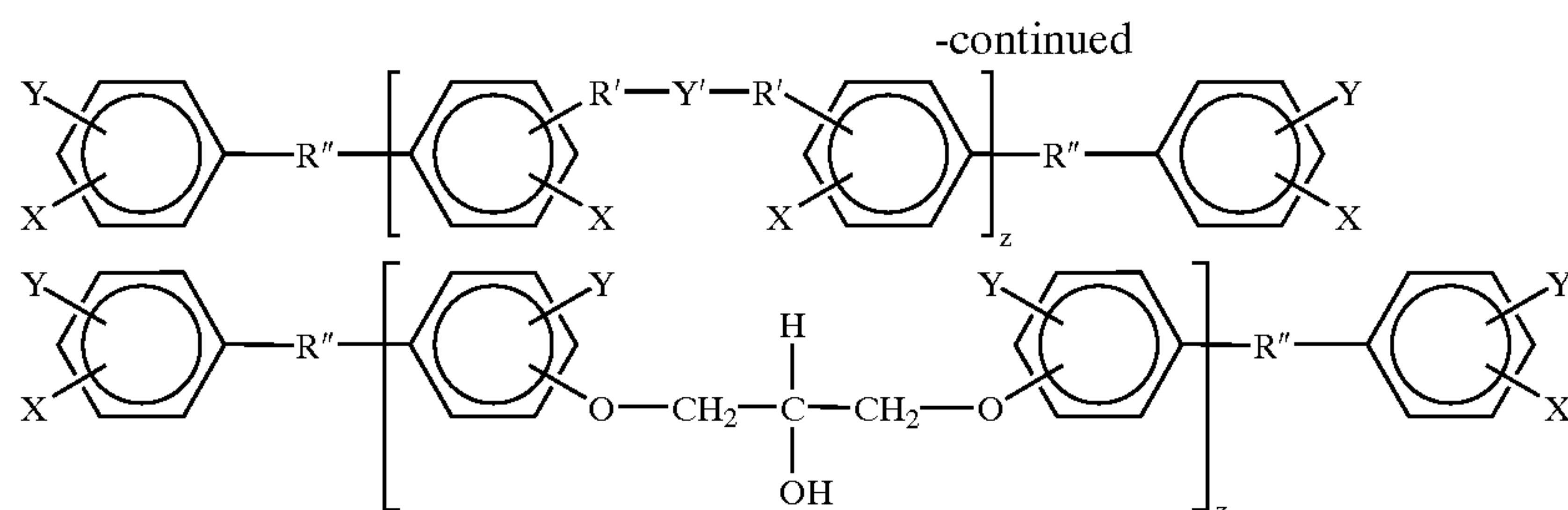
As component (C), compounds containing at least one hydrogen atom attached to a silicon atom (i.e., Si—H group) in the molecule are preferred. Often organosilicon compounds, such as organosilanes and organosiloxanes, having at least one Si—H group, usually 1 to about 100, preferably 1 to about 50, more preferably about 2 to about 20 Si—H groups in the molecule, and having 1 to 500, preferably 1 to 200 silicon atoms are used.

As mentioned above, component (C) used herein is an organic compound or organosilicon compound (such as organosilane and organosiloxane) containing an amount of epoxy group to give an epoxy equivalent of 100 to 5,000 g/mol, and having a phenyl skeleton or at least one benzene ring (as typified by phenyl group), naphthalene ring or anthracene ring as the aromatic ring in the molecule; and preferably an organosilicon compound containing an amount of epoxy group to give an epoxy equivalent of 100 to 5,000 g/mol, having a phenyl skeleton or at least one benzene ring (as typified by phenyl group), and having at least one Si—H group in the molecule. It is noted that JP-A 6-172738 corresponding to U.S. Pat. No. 5,405,896 and JP-A 8-53661 corresponding to U.S. Pat. No. 5,536,803, both of Shin-Etsu Chemical Co., Ltd., disclose an adhesive silicone rubber composition and a silicone adhesive composition, respectively, which contains a tackifier component having a phenyl skeleton or benzene ring (as typified by phenyl group) in the molecule, but not an epoxy group. These adhesive silicone rubber compositions are insufficiently adherent to thermoplastic resins such as polymethyl methacrylate, polyphenylene sulfide, polyamide and polyphthalamide. Separately, compositions comprising a tackifier component having Si—H groups and epoxy groups are known in the art, but this tackifier component does not include a phenyl skeleton or a benzene ring structure (as typified by phenyl group) in the molecule. These compositions fail to achieve sufficient adhesion to the aforementioned thermoplastic resins as well.

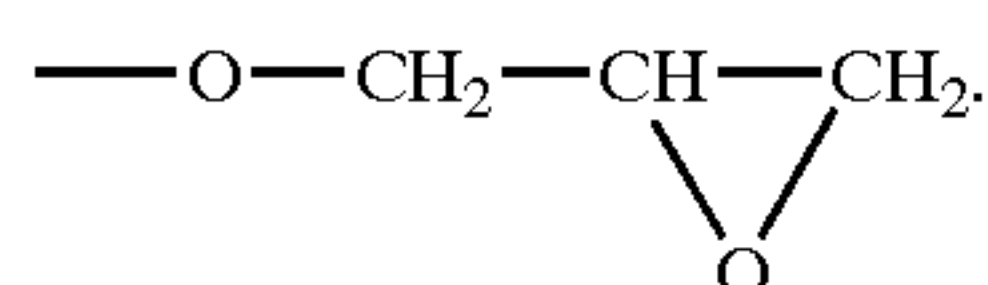
Illustrative examples of the compound (C) used herein are given below.



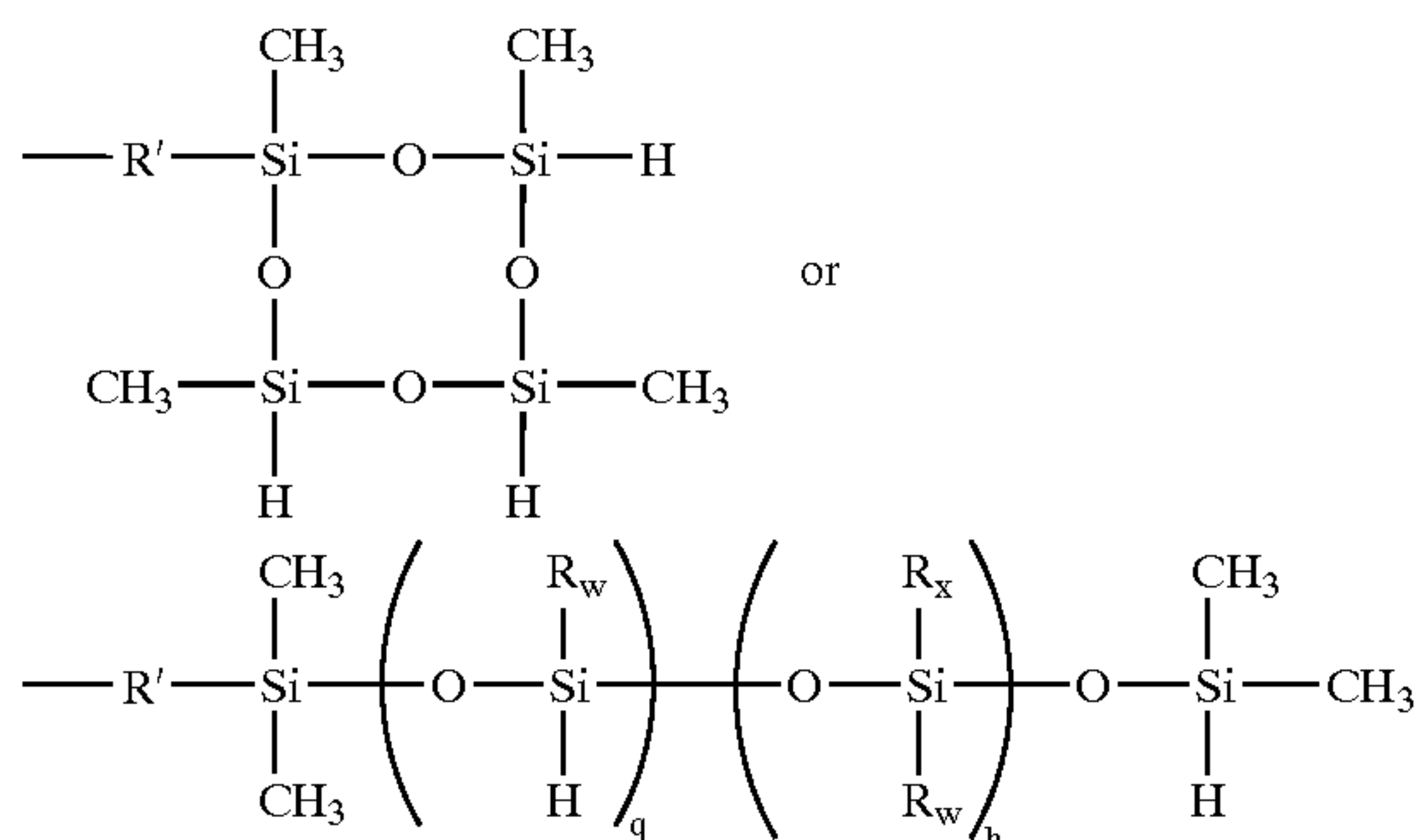




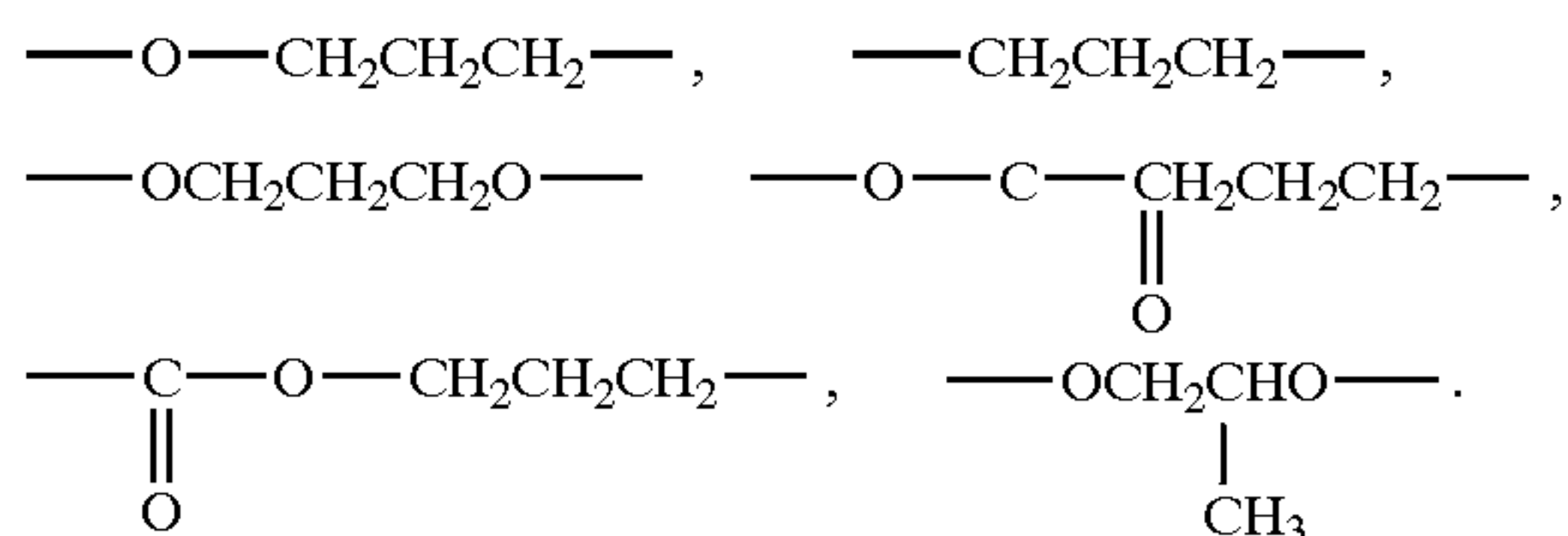
In the formulae, X is



Y is

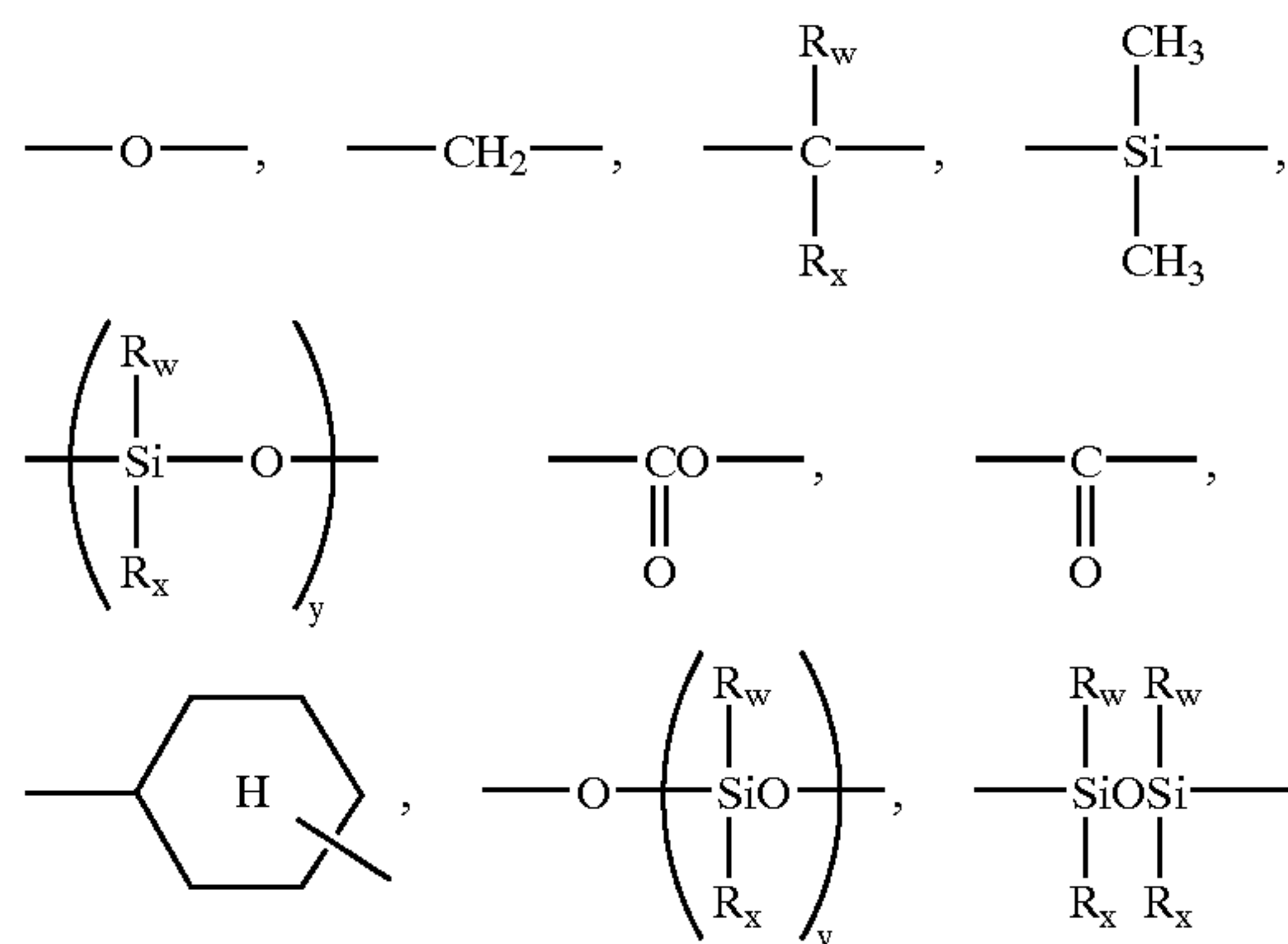


wherein R' is selected from the following groups:



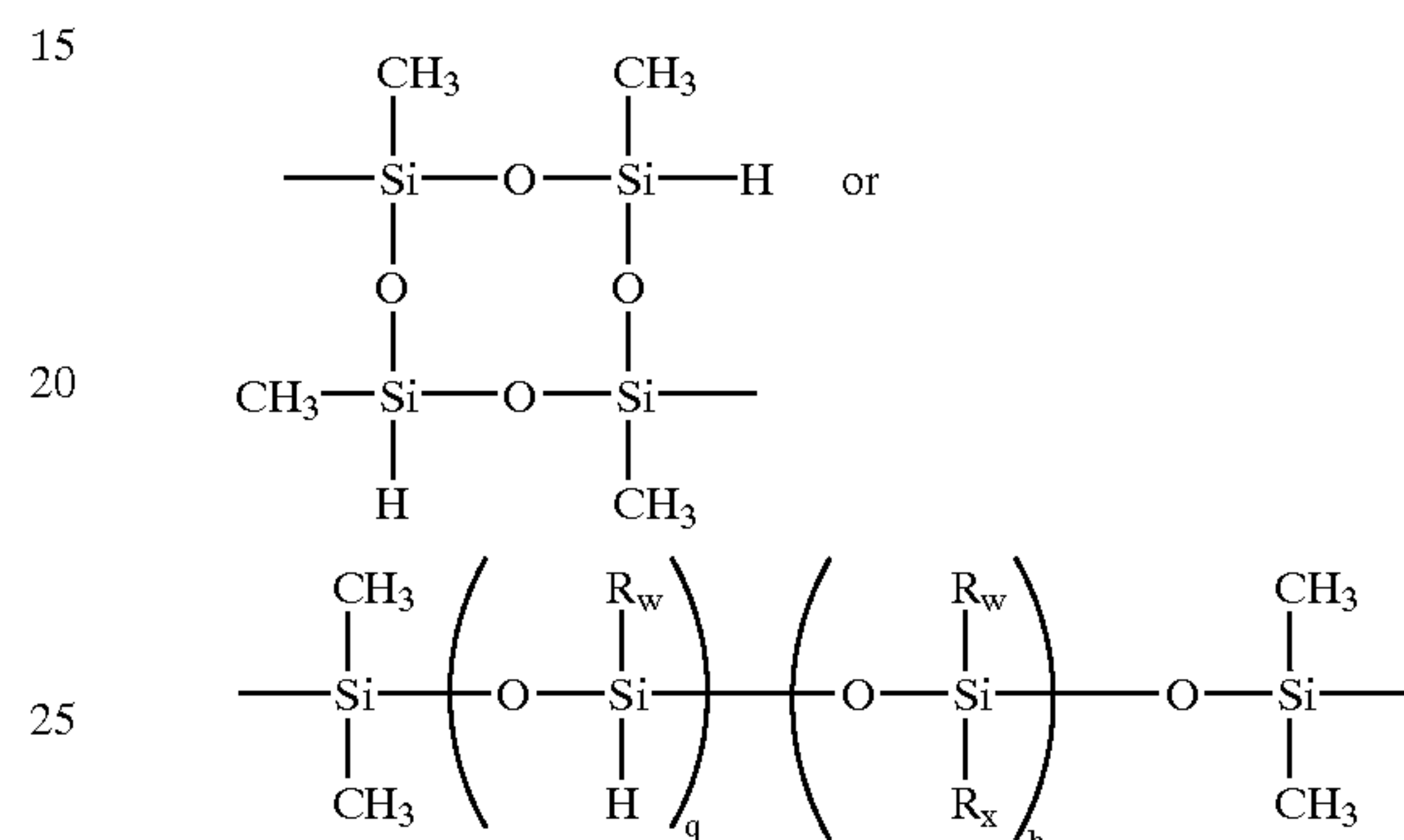
Rw and Rx are substituted or unsubstituted monovalent hydrocarbon groups, q is a number of 1 to 50, preferably 1 to 20, and h is a number of 0 to 50, preferably 1 to 100.

R" is selected from the following groups:



wherein  $R_w$  and  $R_x$  are as defined above, and  $y$  is a number of 0 to 100.

$Y''$  is



wherein  $R_w$ ,  $R_x$ ,  $q$  and  $h$  are as defined above. Subscript  $z$   
30 is a number of 1 to 10.

Also useful are the organic compounds or organosilicon compounds obtained by incorporating alkoxysilyl groups (e.g., trimethoxysilyl, triethoxysilyl or methyldimethoxysilyl), acrylic, methacrylic, ester, carboxyl anhydride, amino or amide groups in the above-enumerated compounds.

More specifically, the substituted or unsubstituted monovalent hydrocarbon groups represented by R<sup>w</sup> and R<sup>x</sup> are preferably those of 1 to 12 carbon atoms, especially 1 to 40 8 carbon atoms. Examples include alkyl, aryl, aralkyl, alkenyl and other groups as enumerated for R<sup>1</sup>. Exemplary substituted monovalent hydrocarbon groups are those substituted with alkoxy, acrylic, methacrylic, acryloyl, methacryloyl, amino and alkylamino groups.

45 As the tackifier component, the above-enumerated compounds may be used alone or in admixture. The reaction product of the above-enumerated compounds is also useful.

An appropriate amount of the tackifier component (C) blended is 0.1 to 50 parts by weight per 100 parts by weight of the organopolysiloxane composition (A). With less than 0.1 part of component (C), sufficient adhesion is not accomplished. More than 50 parts of component (C) can degrade physical properties. The preferred amount is 0.2 to 30 parts by weight.

For the purpose of effectively assisting the tackifier component (C), an organic compound or organosilicon compound having one alkenyl group and at least one ester group in a molecule may be blended. Examples are organic compounds or organosilicon compounds having incorporated therein unsaturated carboxylic acids such as acrylic acid, methacrylic acid and vinylacetic acid, and allyl esters such as allyl benzoate, diallyl phthalate, tetraallyl pyromellitate, and alkyl acid allyl esters. It is also acceptable to add epoxy ring-opening catalysts such as organometallic chelates, amines, amides, imidazoles and acid anhydrides. These aids are added in such amounts that the benefits of the invention are not impaired.



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Besides, a siloxane skeleton-bearing organosilicon compound incompatible with component (A) may be added for the purpose of improving adhesion. Examples include phenyl group-bearing silicone oil, fluorosilicone oil, silicone-modified perfluoroalkyl ether compounds, polyether-modified silicone oil, amino-modified silicone oil, amide-modified silicone oil, imide-modified silicone oil, and urethane-modified silicone oil.

To impart an oil bleeding ability to the inventive composition, at least one non-functional organopolysiloxane having phenyl groups may be added in an amount of about 1 to 20 parts per 100 parts by weight of component (A).

In addition to the above-described components, various additives may be added to the silicone rubber adhesive composition of the invention. Such additives are selected for a particular purpose. Typical additives are metal oxides and compounds thereof such as titanium oxide, iron oxide, cerium oxide, vanadium oxide, cobalt oxide, chromium oxide, and manganese oxide, and inorganic fillers, for example, quartz powder, diatomaceous earth, calcium carbonate, magnesium carbonate, alumina, and carbon. Also, pigments, heat resistance modifiers, flame retardants, plasticizers, and reaction regulators may be added insofar as the desired properties are not impaired. These optional additives may be added in conventional amounts that would not hamper the benefits of the invention.

In the embodiment wherein the addition curing type organopolysiloxane composition is used as (A), an addition reaction regulator may be added insofar as the objects of the invention are not impaired. Suitable regulators are vinyl group-bearing organopolysiloxanes such as vinylcyclotetrasiloxane, triallyl isocyanate, alkyl maleates, acetylene alcohols such as ethynyl cyclohexanol, silanes, modified siloxanes, hydroperoxides, tetramethylethylenediamine, benzotriazole and mixtures of any.

The silicone rubber adhesive composition of the invention can be obtained simply by uniformly admixing the above-described components (A) to (C) and optional components at room temperature. Preferably, component (B) is mixed with component (A) excluding (2) and (3) or (ii) in a planetary mixer or kneader where they are heat treated at a temperature of 100 to 200° C. for 1 to 4 hours, during which period the second surface treating agent may be added. Thereafter, at room temperature, the mixture is admixed with components (2) and (3) or (ii) of component (A) and component (C), thereby obtaining the composition. Any desired molding technique may be selected depending on the viscosity of the mixture or composition. Any of casting, compression molding, injection molding, extrusion molding, and transfer molding techniques is useful. The composition may be heat molded, typically at a temperature of about 60 to 200° C. for about 10 seconds to about 24 hours.

The silicone rubber adhesive composition of the invention is advantageously used in forming integrally molded articles with organic resins. The organic resins used in combination with the silicone rubber adhesive composition are thermoplastic resins of polymerized or polycondensed olefin family, for example, acrylonitrile-butadiene-styrene (ABS) resins, styrene resins, polyethylene resins, polypropylene resins, polyacetal resins, acrylic resins, polycarbonate (PC) resins, polyethylene terephthalate resins, polybutylene terephthalate (PBT) resins, polyphenylene oxide resins, phenolic resins, epoxy resins, polyphenylene sulfide resins, polysulfone resins, nylon resins, aromatic polyamide resins, polyimide resins, liquid crystal resins, and mixtures thereof. They may also take the form of fibers or film.

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Several methods may be employed in integrally molding the uncured silicone rubber adhesive composition on the thermoplastic resin. In one method, a desired shape of the uncured silicone rubber adhesive composition is placed on a preform of the thermoplastic resin, followed by heating at a temperature below the melting temperature of the thermoplastic resin. Another method is by placing the uncured silicone rubber adhesive composition on a preform of the thermoplastic resin, followed by compression at a temperature below the melting temperature of the thermoplastic resin. A further method is by previously injection molding the thermoplastic resin in a mold by means of an injection molding machine, and heat injecting the silicone rubber adhesive composition into the mold. It is noted that the preform of the thermoplastic resin is conveniently prepared by a well-known method involving pelletizing the thermoplastic resin, injecting the pellets into a mold heated above the softening point of the thermoplastic resin, then cooling the mold below the softening point of the thermoplastic resin. In these molding steps, customary molding machines such as injection molding machines and transfer molding machines can be employed. The mold used herein may be a mold of a metal such as steel or stainless steel which has not been surface treated, or a metal mold which has been surface treated such as by chromium plating or nickel plating.

The silicone rubber adhesive composition in the uncured state may take the form of liquid, putty or paste, with the liquid or paste form being preferred for ease of molding. In order that the silicone rubber adhesive composition firmly bond with the thermoplastic resin, the conditions for curing the silicone rubber adhesive composition should include a temperature and time which do not cause deformation, melting and degradation of the thermoplastic resin. Usually integrally molded articles can be formed under curing conditions of 50 to 150° C. and about 0.2 to 5 hours, especially about 0.4 to 30 minutes, although suitable curing conditions vary with the type of resin.

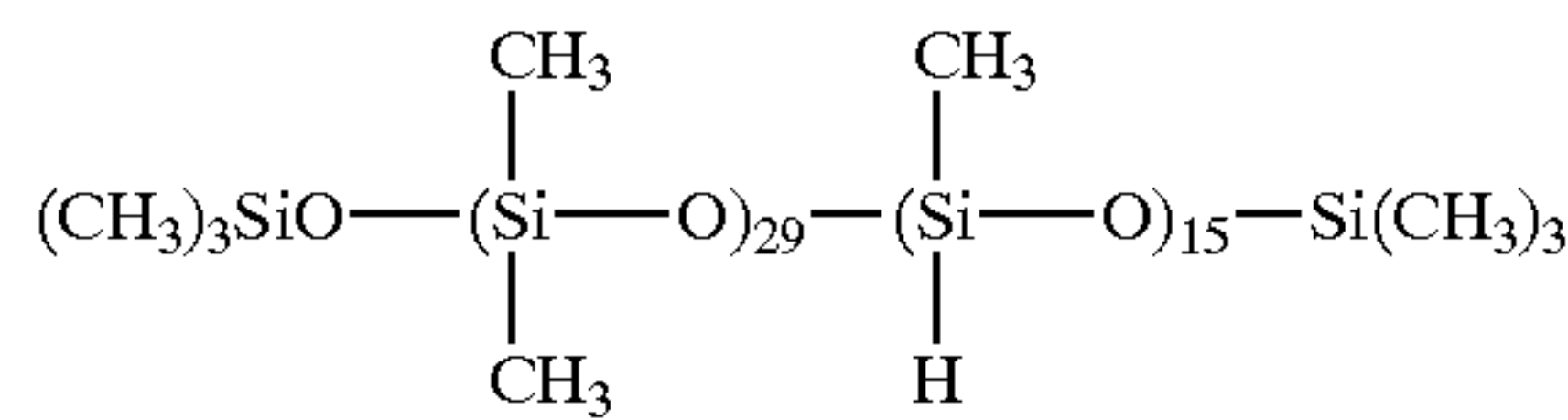
In connection with an integrally molded article of a silicone rubber adhesive composition and a thermoplastic resin, the silicone rubber adhesive composition of the invention is easily moldable within a short time by injection molding, suitable in primerless molding, and bondable with the thermoplastic resin. A bond between the silicone rubber and the thermoplastic resin is achieved without a need for modification of the resin. The integrally molded articles are useful in the electric, electronic, automotive, precision machinery and building fields.

## EXAMPLE

Examples of the invention are given below by way of illustration and not by way of limitation. All parts are by weight.

## Preparation Examples of Silicone Rubber Adhesive Compositions

As shown in Table 1, a dimethylpolysiloxane blocked with a dimethylvinylsiloxy group at each end and having a viscosity of 10,000 centipoise at 25° C. as component (1) of component (A) and fumed silica having a specific surface area of 200 m<sup>2</sup>/g as component (B) were blended together with 8 parts per 100 parts of component (1) of hexamethyldisilazane and uniformly admixed in a kneader/mixer, and further heat admixed at 150° C. for one hour, obtaining a silicone rubber base. To the silicone rubber base were added methylhydrogenpolysiloxane of the average compositional formula (4):



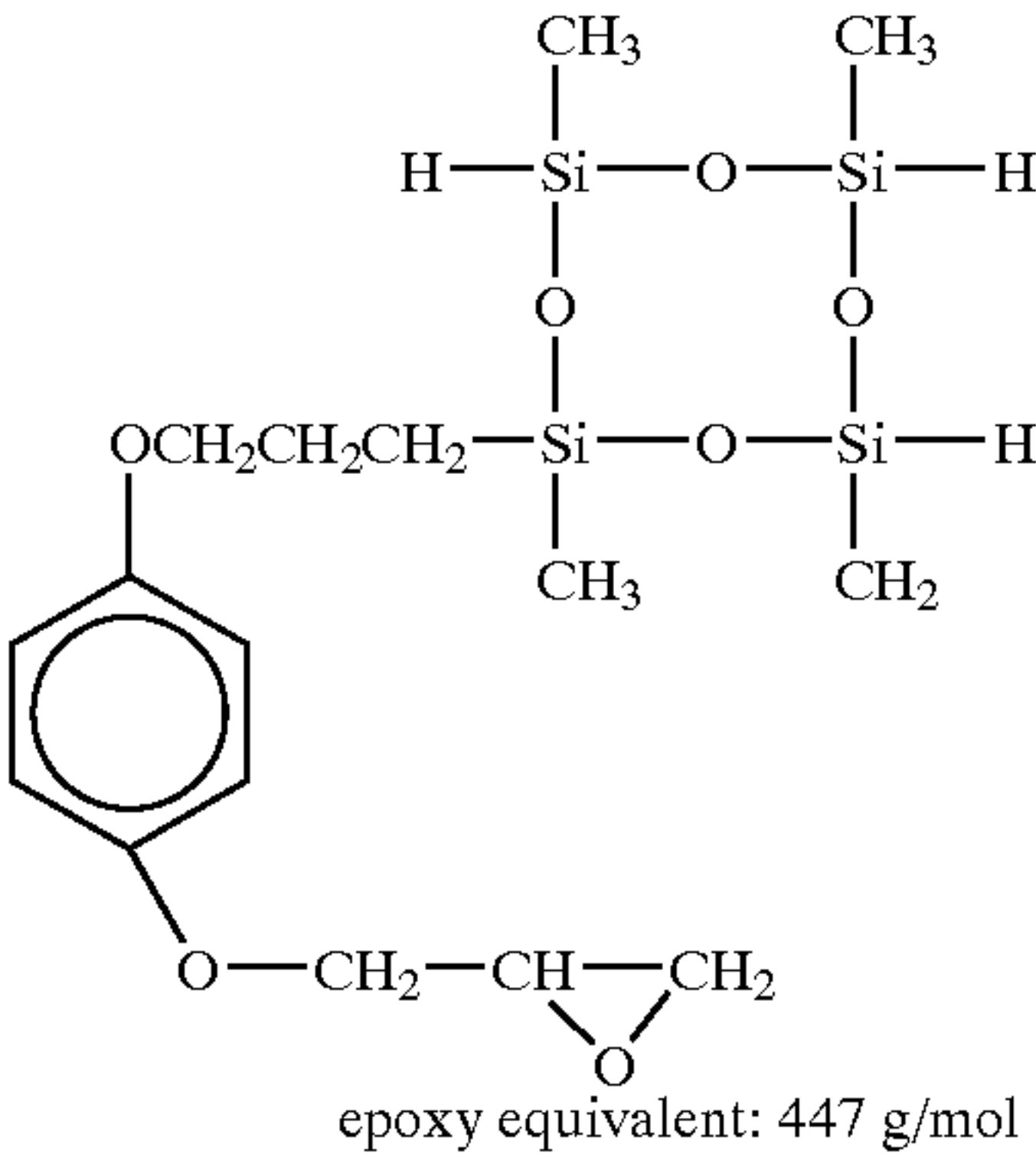
(4)

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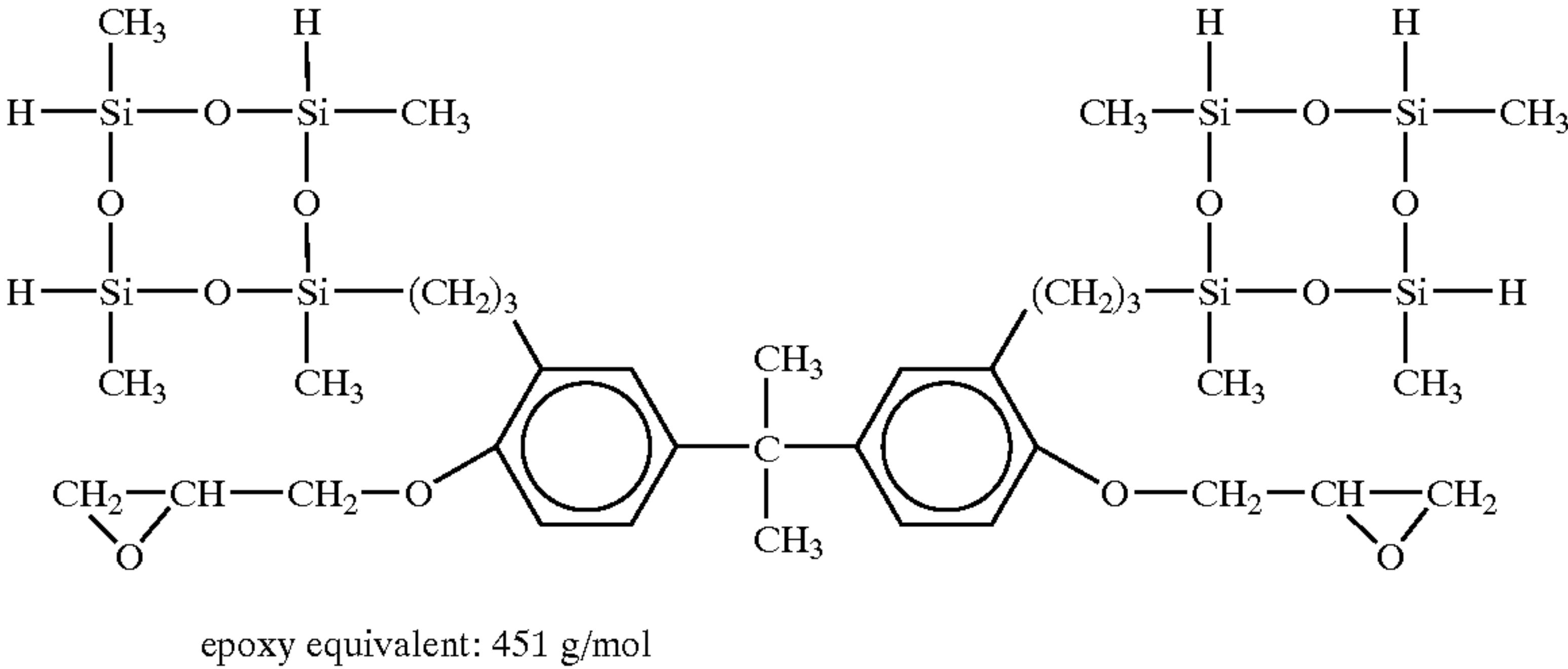
as component (2) in component (A), a 1% 2-ethylhexanol solution of chloroplatinic acid as component (3), and a 50% ethanol solution of ethynyl cyclohexanol as a reaction regulator. Further, tackifier I to IV as component (C) was added. They were uniformly mixed, yielding a silicone rubber adhesive composition.

Component (C)

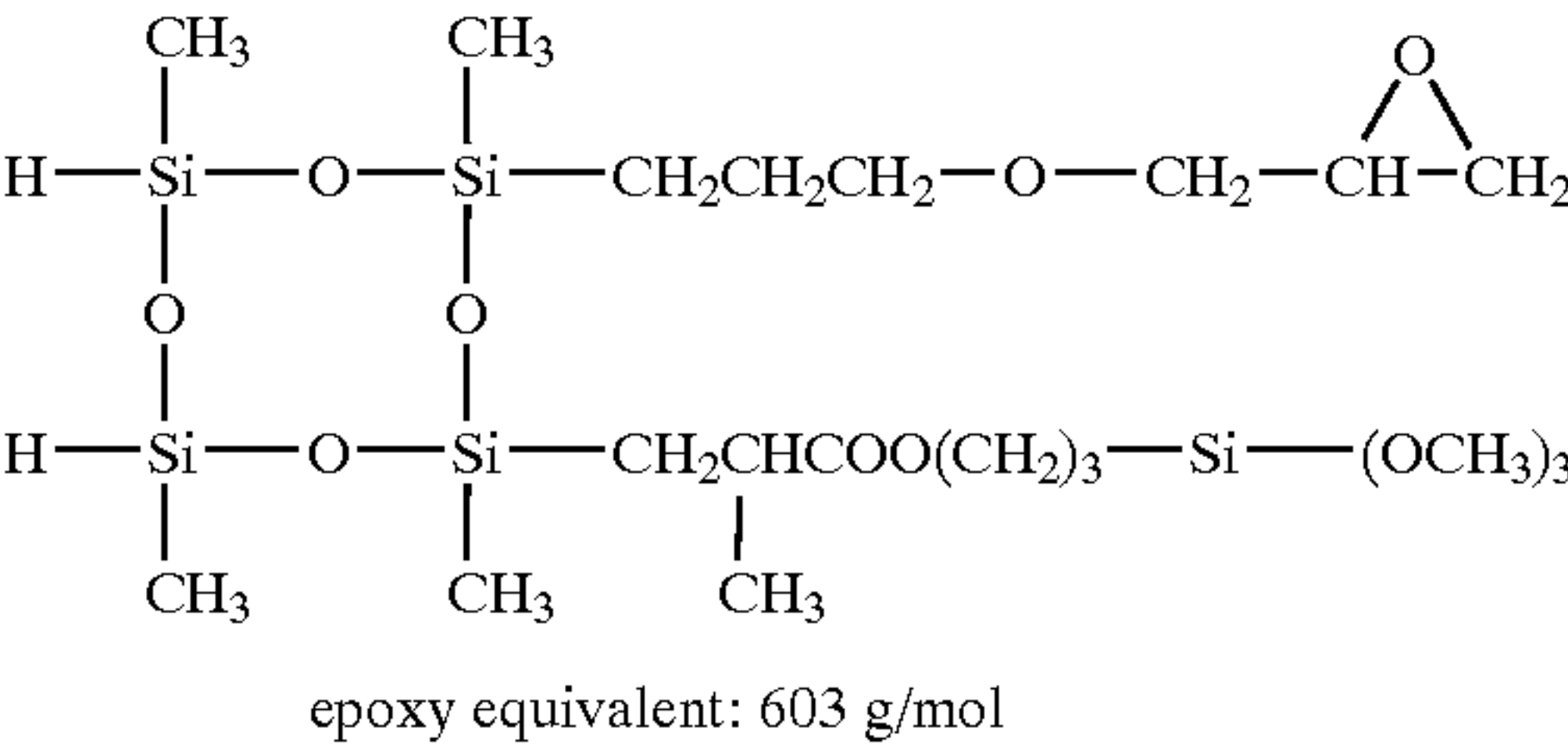
Tackifier I



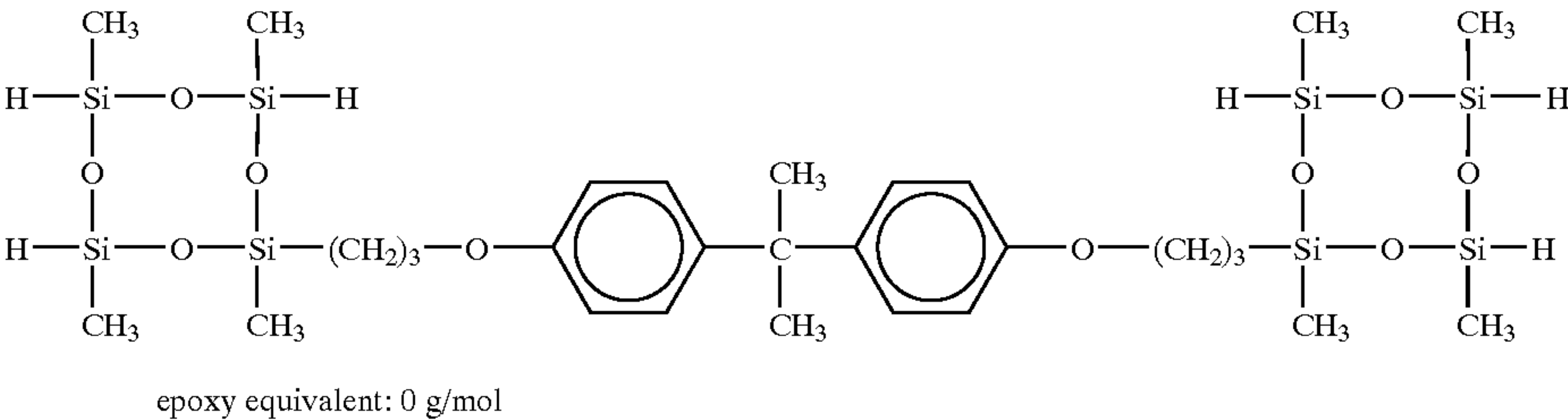
Tackifier II



Tackifier III



Tackifier III





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## Example 1

A thermoplastic resin injection molding machine was used. A polycarbonate (PC) resin having a number average molecular weight of about 10,000, polybutylene terephthalate (PBT) resin having a number average molecular weight of about 20,000, polymethyl methacrylate (PMMA) resin, polyphenylene sulfide (PPS) resin, nylon 6-6 (PA66), and polyphthalamide (PPA) each were admitted into the machine, plasticized at 290° C. and injected into a plurality of cavities in a multiple sheet mold, forming resin sheets of 25 mm×100 mm×2 mm (thick). The injection conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kg/cm<sup>2</sup>, a clamping pressure of 35 ton, and a cavity temperature of 100° C.

Each resin sheet and a chromium-plated metal plate of the same size were secured to a tensile shear bond strength test specimen-forming jig. An appropriate amount of the silicone rubber adhesive composition obtained in the above Preparation Example using tackifier I as component (C) was flowed into the jig, which was heated for 10 minutes in a thermostat tank at 120° C. for curing. A test specimen as shown in FIG. 1 was obtained in this way and examined for bond strength according to JIS K-6850.

In FIG. 1, “a” and “b” designate resin sheets, “c” and “d” are holder clamps, and “e” is the cured silicone rubber adhesive composition.

## Example 2

The resins used in Example 1 each were admitted into the injection molding machine, plasticized at 290° C. and injected into a plurality of cavities in the multiple sheet mold, forming resin sheets of 25 mm×100 mm×2 mm (thick). The injection conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kg/cm<sup>2</sup>, a clamping pressure of 35 ton, and a cavity temperature of 100° C.

Each resin sheet and a chromium-plated metal plate of the same size were secured to the tensile shear bond strength test specimen-forming jig. An appropriate amount of the silicone rubber adhesive composition obtained in the above Preparation Example using tackifier II as component (C) was flowed into the jig, which was heated for 10 minutes in a thermostat tank at 120° C. for curing. A test specimen as shown in FIG. 1 was obtained in this way and examined for bond strength according to JIS K-6850.

## Comparative Example 1

The resins used in Example 1 each were admitted into the injection molding machine, plasticized at 290° C. and injected into a plurality of cavities in the multiple sheet mold, forming resin sheets of 25 mm×100 mm×2 mm (thick). The injection conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kg/cm<sup>2</sup>, a clamping pressure of 35 ton, and a cavity temperature of 100° C.

Each resin sheet and a chromium-plated metal plate of the same size were secured to the tensile shear bond strength test specimen-forming jig. An appropriate amount of the silicone rubber adhesive composition obtained in the above Preparation Example using tackifier III as component (C) was flowed into the jig, which was heated for 10 minutes in a thermostat tank at 120° C. for curing. A test specimen as shown in FIG. 1 was obtained in this way and examined for bond strength according to JIS K-6850.

## Comparative Example 2

The resins used in Example 1 each were admitted into the injection molding machine, plasticized at 290° C. and

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injected into a plurality of cavities in the multiple sheet mold, forming resin sheets of 25 mm×100 mm×2 mm (thick). The injection conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kg/cm<sup>2</sup>, a clamping pressure of 35 ton, and a cavity temperature of 100° C.

Each resin sheet and a chromium-plated metal plate of the same size were secured to the tensile shear bond strength test specimen-forming jig. An appropriate amount of the silicone rubber adhesive composition obtained in the above Preparation Example using tackifier IV was flowed into the jig, which was heated for 10 minutes in a thermostat tank at 120° C. for curing. A test specimen as shown in FIG. 1 was obtained in this way and examined for bond strength according to JIS K-6850.

## Example 3

Molding of the resin and the silicone rubber composition used in Example 2 was carried out using a two-color injection molding machine equipped with two injection cylinders. In this molding machine, nozzles 1 and 2 of the injection cylinders are connected to a mold as shown in FIG. 2. The nozzle 1 is aligned with a mold parting line whereas the nozzle 2 is designed to inject the material into a cavity from its center on the right side of the mold. The mold consists of a left mold half 3 and a right mold half 4. Two recesses are formed in opposed surfaces of the mold halves 3 and 4 so that the recesses may define two cavities 5 and 6 when the mold halves are mated together.

Using this injection molding machine, each resin was melted at 290° C. and injected into the first cavity 5 through the nozzle 1 to form a resin sheet 7 (see FIG. 3). The injection conditions included an injection time of 6 seconds, a cooling time of 35 seconds, and a temperature of 100° C. for both the cavity 5 and the left mold half 3.

Next, the right mold half 4 was moved apart to open the mold, the left mold half 3, with the molded resin sheet 7 held in its recess, was rotated 180°, and the right mold half 4 was moved back. The mold halves were clamped again. At this point, a cavity for molding a silicone rubber sheet was defined between the (lower) recess in the right mold half 4 and the opposing surface of the molded resin sheet 7 as shown in FIG. 4.

In this state, the silicone rubber adhesive composition used in Example 1 (whose recipe is shown in Table 1) was injected from the nozzle 2 against the surface of the molded resin sheet 7, forming a rubber sheet 8 (see FIG. 5). The injection conditions included an injection time of 6 seconds, a cooling time of 90 seconds, a temperature of 100° C. for the left mold half 3, and a temperature of 120° C. for the right mold half 4.

In this way, there was obtained a composite body of the resin sheet 7 bonded to the rubber sheet 8 as shown in FIG. 6. It is noted that both resin and rubber sheets were dimensioned 2.5 mm×150 mm×2 mm (thick). Mold release, dimensional precision and productivity were satisfactory. Adhesion was also examined.

The test results are shown in Table 1.

It is noted that the bond strength was examined by a tensile shear bond strength test according to JIS K-6850. Specimens showing a bond strength of 25 kgf/cm<sup>2</sup> or higher were rated “Bonded.”



TABLE 1

Component	Example			Comparative Example	
	1	2	3	1	2
(pbw)					
(A)					
(1) Dimethylpolysiloxane	100	100	100	100	100
(2) Methylhydrogenpoly-siloxane	5	5	5	5	5
(3) Platinum catalyst	0.1	0.1	0.1	0.1	0.1
Reaction regulator	0.05	0.05	0.05	0.05	0.05
(B)	40	40	40	40	40
Silica fines					
(C)					
Tackifier I	5				
Tackifier II		5			
Tackifier III			5		
Tackifier IV				5	
Adhesion Resin					5
PC	Bonded	Bonded	Bonded	No	Bonded
PBT	Bonded	Bonded	Bonded	No	Bonded
PMMA	Bonded	Bonded	Bonded	No	No
PPS	Bonded	Bonded	Bonded	No	No
PA66	Bonded	Bonded	Bonded	No	No
PPA	Bonded	Bonded	Bonded	No	No
Metal (mold)	No	No	No	No	No
Cr-plated					

What is claimed is:

1. A silicone rubber adhesive composition used for forming an integrally molded article with a thermoplastic resin comprising

- (A) 100 parts by weight of a heat curable organopolysiloxane composition,
- (B) 1 to 100 parts by weight of reinforcing silica fines, and
- (C) 0.1 to 50 parts by weight of an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule

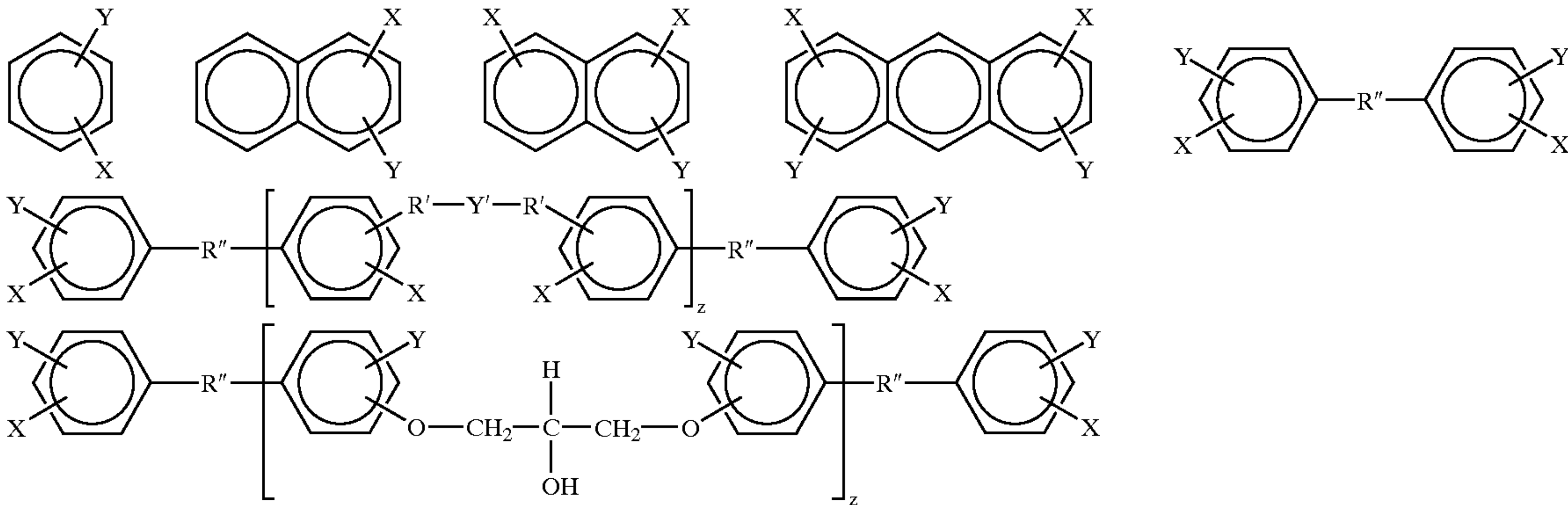
wherein a cured product of said silicone rubber adhesive composition provides a greater bond strength to said thermoplastic resin than any metal mold used for forming the integrally molded article.

2. The composition of claim 1 wherein compound (C) is an organosilicon compound containing at least one Si-H group in a molecule.

3. The composition of claim 1 which provides a greater bond strength to organic thermoplastic resins than to steel.

4. The composition of claim 1 wherein the organosilicon compound has at least one linear or cyclic siloxane structure.

5. The composition of claim 1 or wherein compound (C) is at least one selected from the compounds of the following formulae:

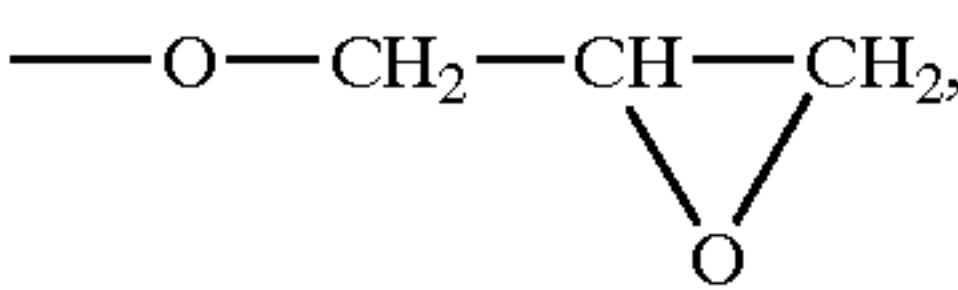


It is evident from Table 1 that silicone rubber adhesive compositions within the scope of the invention can be briefly cured to various resins to form integrally molded articles in which the silicone rubber is firmly bonded to the resin. Additionally mold release, dimensional precision and productivity are satisfactory.

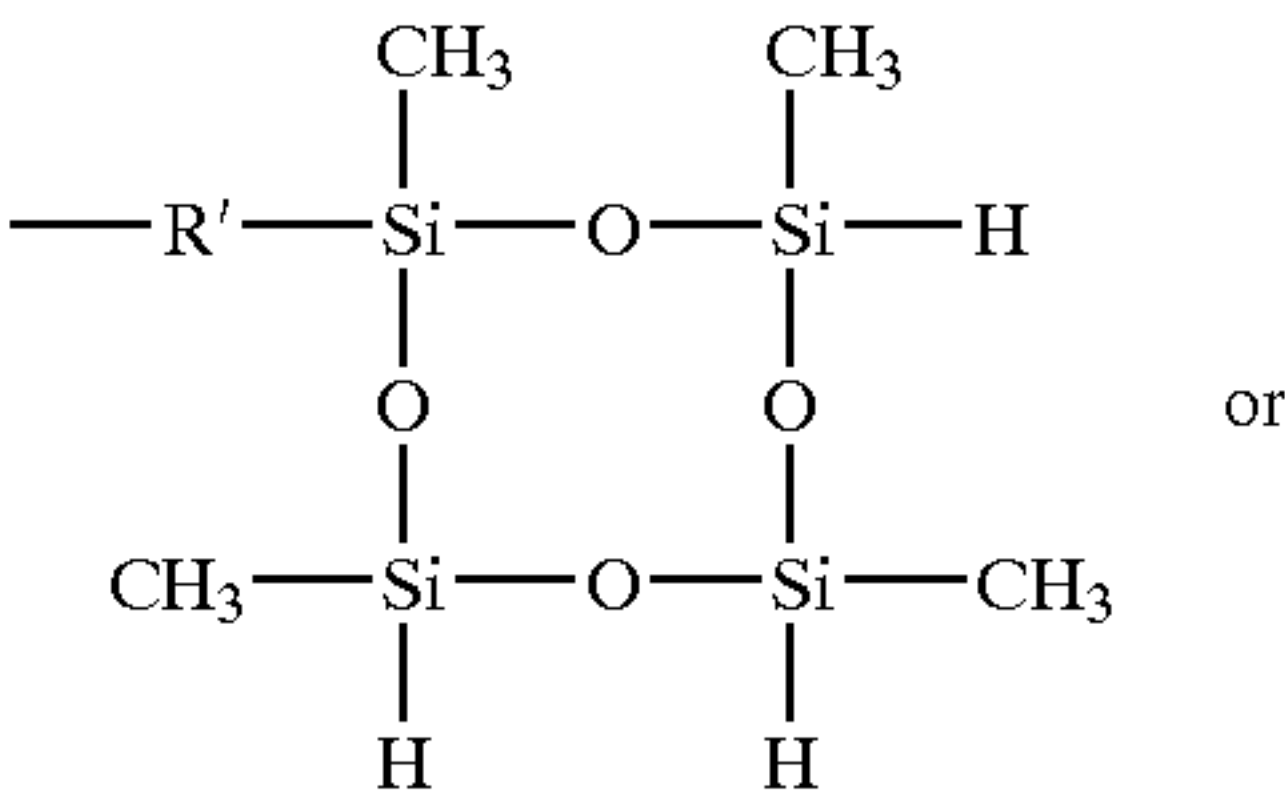
Japanese Patent Application No. 2001-000536 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

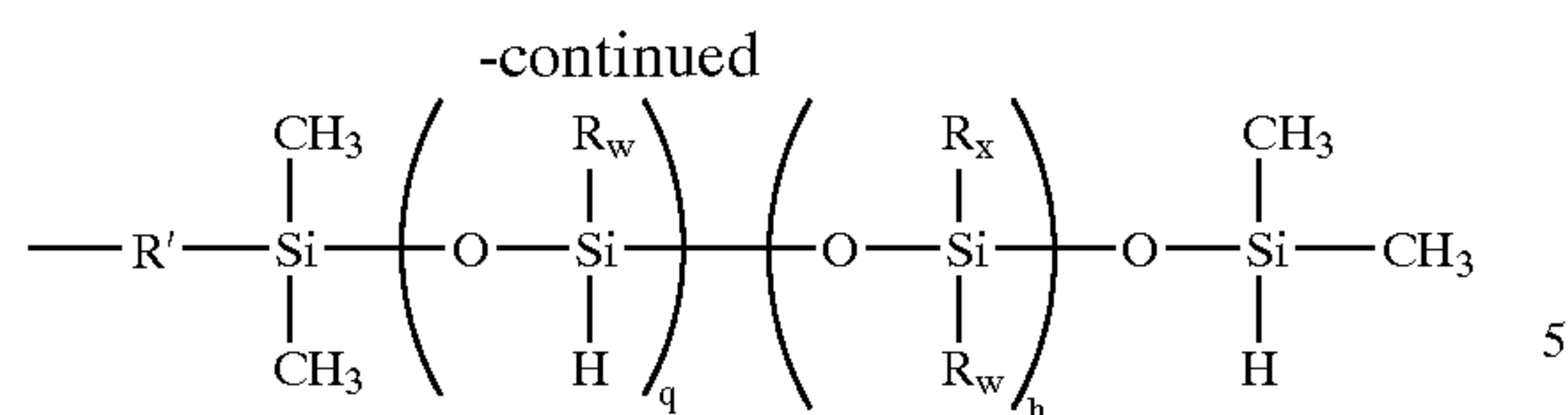
wherein X is



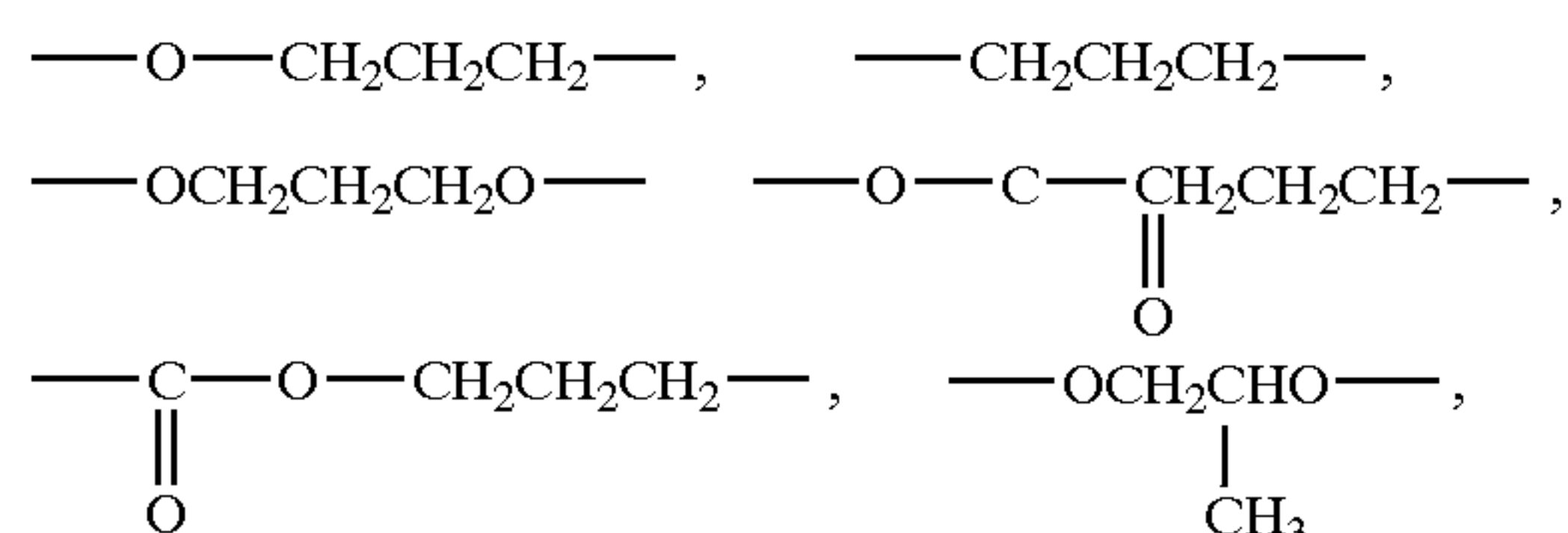
Y is



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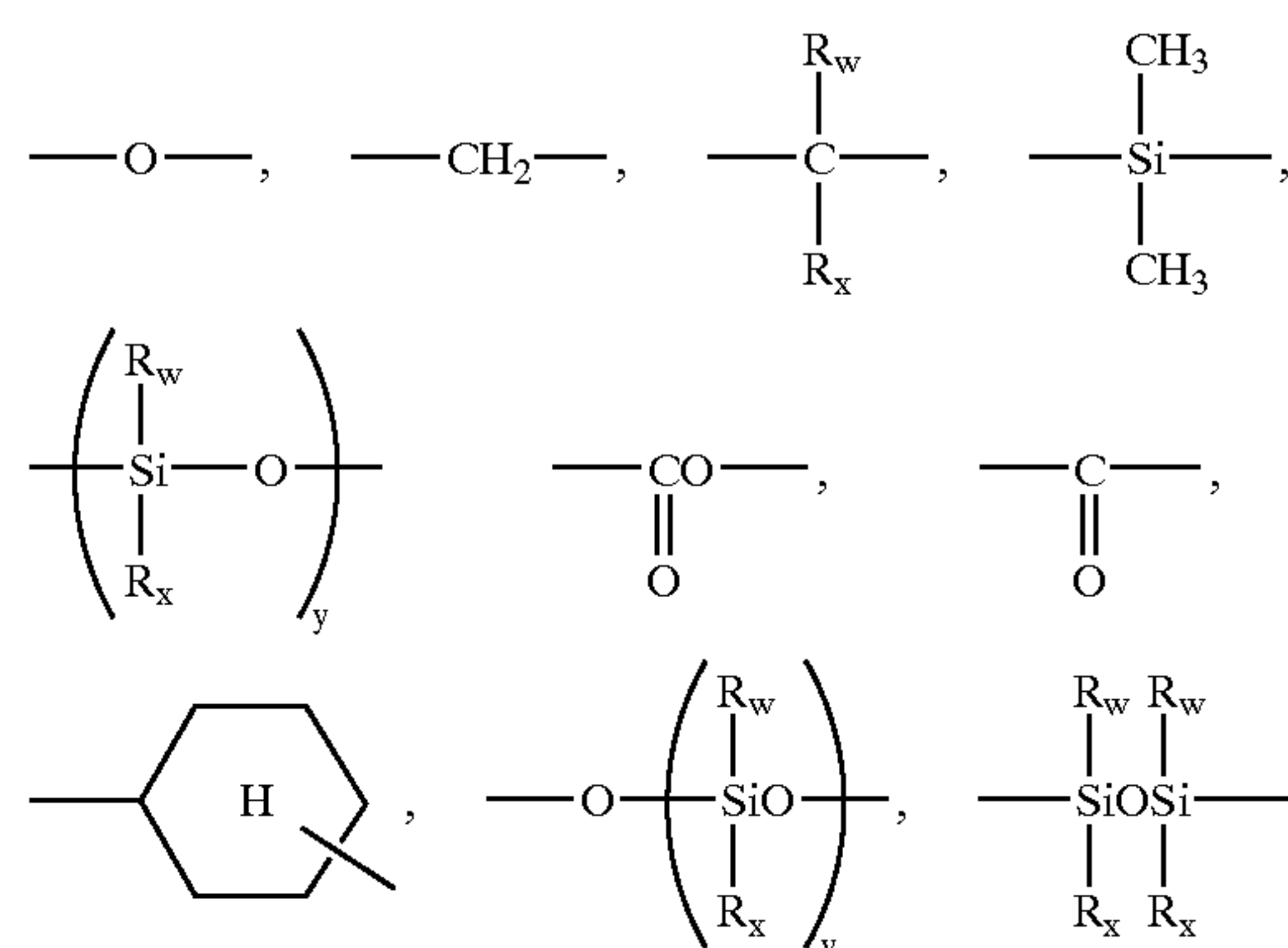


wherein R' is selected from the following groups:



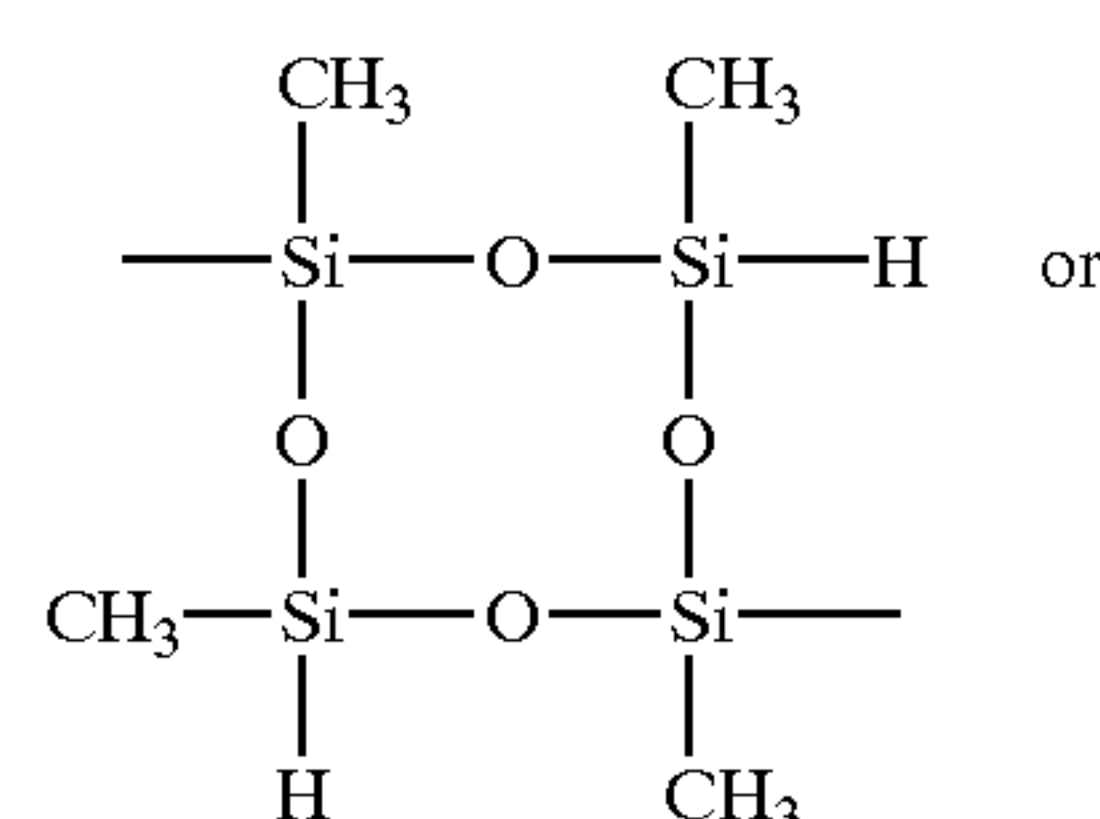
R<sub>w</sub> and R<sub>x</sub> are substituted or unsubstituted monovalent hydrocarbon groups, q is a number of 1 to 50, and h is a number of 0 to 50,

R' is selected from the following groups:

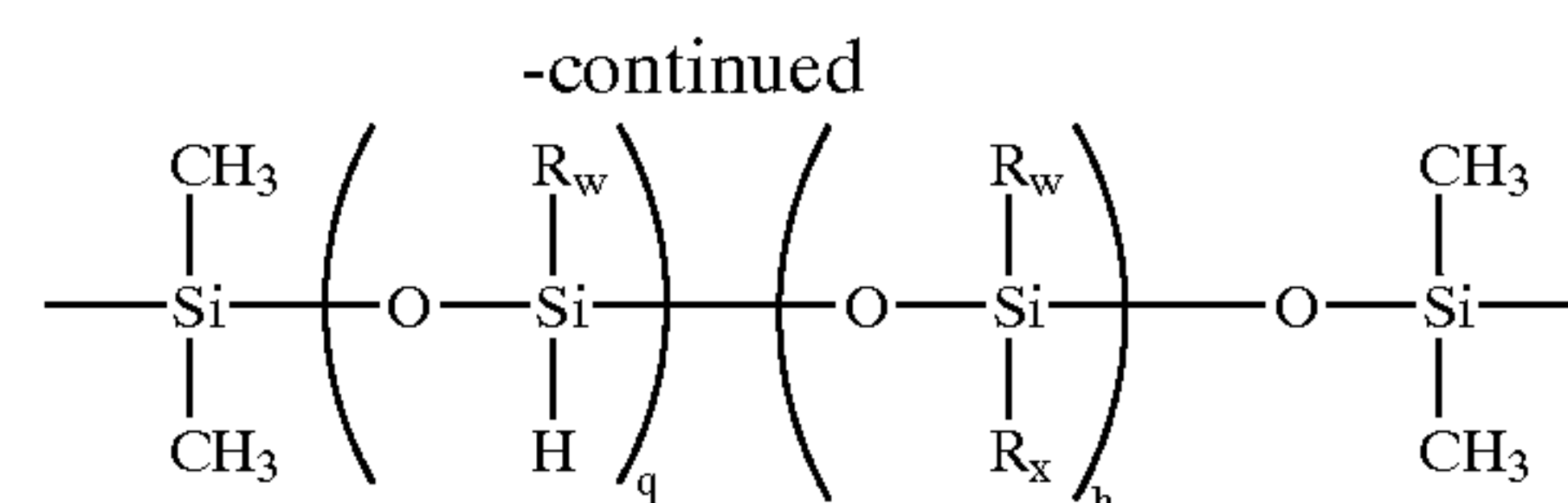


wherein R<sub>w</sub> and R<sub>x</sub> are as defined above, and y is a number of 0 to 100, and

Y is



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wherein R<sub>w</sub>, R<sub>x</sub>, q and h are as defined above and Subscript z is a number of 1 to 10.

6. The composition of claim 1 wherein the organopolysiloxane composition comprises a diorganopolysiloxane of a straight chain structure whose backbone comprises recurring diorganosiloxane units of the formula: R<sup>1</sup><sub>2</sub>SiO<sub>2/2</sub> and which is blocked with a triorganosiloxy group of the formula: R<sup>1</sup><sub>3</sub>SiO<sub>1/2</sub> at either end

wherein R<sup>1</sup> is a substituted or unsubstituted monovalent hydrocarbon group of 1 to 12 carbon atoms.

7. The composition of claim 1 wherein the organopolysiloxane composition comprises a diorganopolysiloxane has a weight average degree of polymerization of about 10 to 10,000.

8. An integrally molded article comprising a silicone rubber adhesive composition in the cured state and a thermoplastic resin, said silicone rubber adhesive composition comprising

(A) 100 parts by weight of a heat curable organopolysiloxane composition,

(B) 1 to 100 parts by weight of reinforcing silica fines, and

(C) 0.1 to 50 parts by weight of an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule.

9. An integrally molded article comprising a silicone rubber adhesive composition in the cured state and a thermoplastic resin, said silicone rubber adhesive composition comprising:

(A) 100 parts by weight of a heat curable organopolysiloxane composition,

(B) 1 to 100 parts by weight of reinforcing silica fines, and

(C) 0.1 to 50 parts by weight of an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule

wherein compound (C) is an organosilicon compound containing at least one Si—H group in a molecule.

10. A silicone rubber adhesive composition used for forming an integrally molded article with a thermoplastic resin comprising:

(A) 100 parts by weight of a heat curable organopolysiloxane composition,

(B) 1 to 100 parts by weight of reinforcing silica fines, and

(C) 0.1 to 50 parts by weight of an organic compound or organosilicon compound having an epoxy equivalent of 100 to 5,000 g/mol and containing at least one aromatic ring in a molecule.

\* \* \* \* \*